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HE CHEMICAL ACTION
of
ULTRAVIOLET RAYS

by

CARLETON ELLIS

and

ALFRED A. WELLS

Revised and Enlarged Edition

by

FRANCIS F. HEYROTH, M.D., Ph.D

University of Cincinnati

BOOK DEPARTMENT

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of mercury discharge tubes. The Atlas Electric Devices Co. and the Nation Carbon Co have furnished numerous illustrations. Many authors and publishe of books and journals, too numerous to mention, have permitted the publication illustrations from their work. Drs. D. A. Wells, W. M. Burgess and the lat Albert Sherman have read certain chapters and offered valuable suggestions. Th authors of the first edition have been especially helpful. Many reference books review articles and incidental summaries, as well as abstracts of patents and o material in difficultly accessible sources, have been freely used. The effort ha been made to acknowledge these in suitable places.

FRANCIS F. HEYROTH.

Institute of Scientific Research
University of Cincinnati
June, 1940

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Chapter 1

Introduction: Nature of Ultraviolet Radiation

The agency of light and the field of photochemistry, aside from photography, have until recently received relatively little use on a commercial scale. To be sure, a few photochemical processes of an industrial character, such as the production of benzyl chloride, have had a limited commercial application, but most chemical operations utilizing the agency of sunlight have been found slow and ineffective. In contrast with the industrial applications, theoretical photochemistry has recently attracted many workers, and a few guiding principles, together with a considerable amount of detailed information, have been obtained during the past three decades. Much of this advance has been due to the study of the effects of ultraviolet radiation which, following the development of suitable sources, has been carried on with vigor.

Everyone is familiar with the application of ultraviolet irradiation methods to the problem of enriching the vitamin D content of milk and of certain other foodstuffs and pharmaceutical products. The number of branches of chemistry in which this radiation has been studied is, however, often a source of surprise to chemists when they first become cognizant of the facts. This is largely because comparatively few industrial operations are carried out with this form of radiant energy.

Foodstuffs, the fuels which supply the energy of all animal life, are built up by the action of sunlight in plants. Desirable as it might be to develop ways of replacing the present farming methods by well-controlled photochemical operations conducted in a factory, this is of less immediate importance than the problem of the exhaustion of natural fuels which serve as sources of energy for our mechanized civilization. Coal and oil represent the stored vegetation of the past. In an address on the future problems of engineering, Parsons[1] pointed out the limitations imposed by thermodynamics upon the utilization of fuels and emphasized the imminent need for studies of the availability of other sources of energy. After considering hydroelectric power sources and the other less explored possible sources of energy such as the atom, the heat of the earth, tides, waves and wind, he concluded that the most promising source is the sun. For the utilization of solar energy it may be necessary to find reactions which will yield compounds of high energy content which can serve as storage reservoirs.

MAGNITUDE OF SOLAR ENERGY

From the time of Joseph Henry, workers at the Smithsonian Institution, including particularly S. P. Langley and, at present, Charles Abbot, have made many measurements of the total amount of energy received on the earth from the sun at a number of stations throughout the world. The solar constant is defined as the solar energy which impinges in unit time on unit area of a surface perpendicular to a sunbeam just outside the earth's atmosphere. Observations made at the earth's surface are corrected for the loss of about 30 per cent which occurs during the passage of the light through the atmosphere. The mean value of the solar constant has been found to be 1.94 calories per minute per square centimeter, equivalent to 1.35×10^6 ergs per square centimeter per second. The fluctuations of 2 to 3 per cent on both sides of the mean appear to be associated with the eleven-year sunspot cycles, the radiation being greatest when the spots are most numerous.

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[1] Parsons, W. B., *J. Frank. Inst*, **200**, 219 (1925).

Stewart[2] has made calculations which enable one to visualize the meaning of these figures in comparison with the amounts of energy available from other sources. He concludes that the sun at the zenith supplies the outer atmosphere with 4,690,000 horsepower per square mile. At the surface this is equivalent to about $4{,}690{,}000 \cos \theta \times (0.70)^{\sec \theta}$ where θ is the angle between the sun and the zenith. The maximum power output of Niagara Falls is estimated at about 4,000,000 H.P. At noon on a clear day in June, the sunlight falling on 133 square miles at Philadelphia is equivalent in power to 100 Niagaras; it is about 70 per cent less in December. If the radiation which strikes the whole earth in a single second could be converted into power, its value, at one cent per kilowatt-hour, would be nearly half a billion dollars. Parsons stated that, assuming the total span of daily sunlight to be equal to nine hours of maximum intensity and 50 per cent of the energy to be recoverable, a strip of land 10 miles wide and 100 miles long would develop daily as much power as could have been obtained from one-half the world's total fuel consumption in 1920, allowing three pounds of coal per horsepower. The area of Salt Lake, Utah, alone would suffice to produce energy equal to that furnished by the whole annual world consumption of coal.

As the earth intercepts only one part in 22,000 millions of the total energy radiated by the sun, it may be calculated that the sun emits nearly 75,000 H.P. per square yard of its surface. At one cent per kilowatt-hour, its power output would be valued at "a billion dollars in a billionth of a second."

Attempts made thus far to utilize this energy have been limited to the use of aqueous vapor as an intermediary in an engine operated by very low steam pressure. According to Parsons, the maximum overall efficiency obtained in the Shuman-Boys absorber in Meadi, Egypt, was 4.32 per cent. As yet few, if any, attempts have been made to concentrate the sun's rays by a system of reflectors upon chemicals in order to get the latter to react to produce others of high energy content and fuel value

The conscious development of such ideas has instead been concentrated largely upon the problem of the mechanism by which chlorophyll enables plants to utilize solar energy in building up the compounds which serve as foods.

NATURE OF RADIANT ENERGY

An understanding of the chemical reactions produced by ultraviolet radiations requires a knowledge of their physical nature. As they represent but one of the forms of radiant energy which comprise what is called the electromagnetic spectrum, there is given in the following portions of this chapter a brief historical sketch of the present knowledge of light, visible and invisible. There is an essential physical unity in the nature of wireless waves, infrared radiation, visible light, ultraviolet radiation, x-rays and gamma-rays. Photochemical changes induced by visible light and by ultraviolet radiations are quite similar in mechanism, differing chiefly in the amounts of energy involved and in the types of equipment necessary.

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[2] Stewart, J. Q., *J Frank. Inst.*, **204**, 438 (1927).

These two forms of radiant energy are distinguished by special names merely because our eyes permit us to appreciate the presence of the visible but not of the ultraviolet radiations.

Since 1913 conceptions derived from the study of the mechanism of the production, transmission and absorption of radiations have come to dominate and transform modern chemistry and physics. They have been applied with great success to the problem of the constitution of the atom, affording models by which to express the facts embodied in the periodic table. Very recently, they have led to new methods of studying the nature and strength of the chemical bond and have given rise to a new attack on the fundamental problem of chemical affinity.

Each of the forms of radiant energy is transmitted through a vacuum at the same rate, 186,000 miles per second or 3×10^{10} centimeters per second, the long-known velocity of light. The manner in which light is transmitted through space has been for more than two centuries the subject of a controversy between the adherents of the wave and corpuscular theories, the origin of neither of which is certain.[3]

The inadequacy of a corpuscular theory to account for the phenomena of diffraction and interference led Huyghens in 1690 to state, without claiming the idea as his own, that light is made up of waves which he conceived as longitudinal pulses extending in all directions from a center of disturbance along a spherical front. He did not, however, conceive of the existence of a train of waves. Newton, the discoverer of the resolution of white light into a spectrum by means of a prism, on the other hand, favored the view that light is transmitted as minute corpuscles ejected through space, since he believed (1672) that a wave theory could not account for the rectilinear propagation of light. He described the phenomena of diffraction of light passing between closely spaced knife edges and the famous rings of color observed in thin plates, now known to be due to interference. Both of these phenomena now, as then, afford the strongest evidence for the wave nature of light. Newton [4] ascribed them to certain "fits" of reflection or transmission. Notwithstanding the fact that Huyghens had shown it possible to explain the rectilinear propagation of light and the phenomena of refraction by certain geometrical constructions regarding the advancing wave form, confusion reigned for about a century.

By extending the wave theory to include a continuous series of periodic waves, Dr. Thomas Young was able to explain the phenomenon of interference and to demonstrate it in a famous experiment in a Bakerian Lecture before the Royal Society in 1801. Light from a single source was made to pass through two very closely adjacent pinholes and illuminate a spot upon a screen. At the spot where the two cones of light overlapped, dark and light bands are observed. Any point within this area receives light by two different paths, one from each pinhole. If the lengths of these paths differ, the crest of a wave reaching it by one path may meet the trough of a wave reaching it by the other; with a different ratio of the lengths of the paths, a spot nearby may receive the crests of both waves. In the former case the crest and trough (then believed to be points of maximum compression and rarefaction) annul each other, are said to interfere, and the spot receives no illumination. In the latter case the waves add together and the spot is very bright.

This experiment regarding the nature of interference turned the tide in favor of the wave theory of light. In the early theory, the waves were conceived as longitudinal compressions and rarefactions of the ether similar to those by which sound is transmitted by air. New difficulties were introduced by the discovery of the phenomenon of the polarization of light (Malus, 1809) and the investigation by Arago of the rotation of the plane of polarization by various substances. These phenomena, unlike any encountered in the case of sound, eluded explanation until Fresnel in 1821 published the brilliant suggestion that the light waves may be vibrations transverse to the direction of propagation of the spherical wave-front.

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[3] Crew, H., *J. Opt. Soc. Am.*, **20**, 6 (1930).

[4] Newton, Sir Isaac, "Optics," 1704.

Wave-length and Its Measurement

1. *Fundamental Concepts and Methods.* The distance from crest to crest or trough to trough of a series of waves is known as the wave-length. For visible light it is very small and must be measured in suitable small units. That the wave-length has for each color a constant and characteristic value was indicated by later interference experiments of Young.

While all colors of light travel at the same rate in a vacuum, this is not the case when they pass through transparent material bodies. In going from a light medium to a denser one the velocity of light is slowed to an extent which depends upon the wave-length. For this reason, white light in passing through a prism is spread out into a spectrum of colors. The greater the thickness of the path of light in the prism the greater the resolution or spreading of the spectral colors. Measurements of the wave-length of light in some limited spectral regions, as for example the yellow, were early made by means of an experimental arrangement based upon the interference of waves reaching a spot along paths of slightly different lengths.

For precise measurements of this sort the particular region at which the measurement is made must be reproducibly defined. Fraunhofer found in the solar spectrum a series of dark lines which serve as natural landmarks for certain wave-lengths, rendering the location of a given point in the spectrum possible irrespective of the resolution of the prism. It was later found that these lines correspond in wave-length to the bright lines found to be superposed on a continuous colored background when certain elements are heated to high temperatures. Kirchhoff found that the elements which emit these lines are also capable of absorbing them when the vapors of the elements are placed between a continuous source and the spectrograph. The theory of the origin of the Fraunhofer lines in the solar spectrum is that certain elements in the gaseous atmosphere of the sun absorb the sun's radiations at just these wave-lengths, and so lessen their brilliance in the solar spectrum.

In 1823 Fraunhofer made precise measurements of the wave-lengths of the chief dark lines which occur in the solar spectrum. He employed for this an instrument based upon the principle of interference, the optical grating. With a diamond, he ruled a great number of equally and very closely spaced parallel lines in a thin film of gold deposited on a glass plate. This grating simulates a prism in its ability to separate the wave-lengths of light; unlike the prism it permits the wave-length of any line to be measured by direct methods described in detail in any textbook on optics.

Because of the likelihood of mechanical imperfections in the ruling of even the best gratings (such as those ruled by Rowland) Michelson, in 1893, turned to the use of interferential apparatus. This represents a simplification of the principle of the diffraction grating, since the many thousands of waves which act simultaneously in grating experiments are, in the interferometer, replaced by but two with a very large difference in path. The interferometer offers resolution practically without limit. Its use showed that spectral lines are often accompanied by other lines called "satellites" and made possible the development of modern theories of the multiplicity of spectral lines.

With the help of Benoit in the Bureau Internationale des Poids et Mésures, Michelson determined the wave-length of the cadmium red line with a precision far beyond that of all previous workers. By the use of a new interferometer, Fabry in 1900 and Perot[5] compared the wave-length of the red cadmium line with the standard meter in Paris and found the wave-length to be equal to 0.00064384696 mm., the observations being taken in dry air at 18°C. and at a mercury pressure of 76 cm. This value agreed well with that of Michelson who reported 0.00064384700 mm. for the same line. Seven years later Fabry and Buisson investigated certain other wave-lengths and from these measurements there developed the international system of wave-lengths, the precision of which is probably one part in a million in absolute as well as in relative values. Standard values for many lines can be found in the "International Tables of Critical Constants" It may at first seem that such precision is unnecessary. Recently, however, numerical relations have been discovered between the wave-lengths of different spectral lines emitted by the same element and these have led to the development of theories of atomic structure. At the present time the details of the structures of individual lines are being actively investigated. This work requires data of high precision.

2. *Units.* The minuteness of the wave-lengths of the colors of visible light makes it desirable to express them in terms of units of length much smaller than the millimeter. In the ultraviolet, and sometimes also in the visible range, the Ångström unit is employed. This is defined as 1×10^{-8} cm. It is commonly abbreviated by the letter A rather than the Swedish Å. The cadmium red line is 6438.4696A. In the visible region many workers employ a unit, ten times as large as the Ångstrom (10A), called the millimicron. A micron is the millionth part of a meter and the millimicron is the thousandth part of this, since *milli* in the metric system means "the thousandth part of" the unit to which the term is prefixed. It is correctly designated by the symbol $m\mu$, since the letter "m" is the standard abbreviation for milli, and μ that for the micron or, in general, "millionth part of."[6]

Another manner of designating or identifying a given radiation is based upon the velocity with which light travels in a vacuum. The number of wave crests which pass a given point in a second, *i.e.*, the frequency of the light, is obtained by dividing the velocity of light expressed in centimeters per second by the wave-length in question expressed in centimeters. Frequencies are of importance in connection with modern views of the mechanism of the emission of light from hot bodies. They involve very large and unwieldy numbers.

Smaller figures may be obtained by dividing the true frequencies by the velocity of light. The units so obtained are known as wave-numbers and represent the number of crests within a distance of one centimeter of a wave-train viewed instantaneously. The wave-number is obviously the reciprocal of the wave-length expressed in centimeters, rather than in Ångström units. It has been much employed in recording the data of spectroscopy.

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[5] This account has been derived largely from an address by Charles Fabry, The Franklin Institute Centenary Lecture, Sept. 17, 1924.

[6] Following Kayser, the German authority on spectroscopy, the millimicron has been abbreviated as $\mu\mu$ by many writers. This is erroneous since it would logically mean the millionth part of the millionth part of a meter. The error was pointed out by Guillaume, director of the International Bureau of Weights and Measures in 1913, but the misleading symbol is still frequently encountered. Camp, J. P., *Science*, **70**, 453 (1929); Dorsey, N. E., *Ibid.*, **71**, 67 (1930).

INVISIBLE RADIATIONS

The visible spectrum covers only the short range of wave-lengths from 7200-7600A at the red end to 3900-4000A at the violet end, the exact limits varying from one person to another, and from one species of animals to another. In 1800, Sir William Herschel discovered that the heating effect of sunlight was not confined to the visible portion of the spectrum from a prism since a thermometer placed beyond the red end where nothing could be seen showed a higher temperature than when exposed to the red rays. About this time the existence of some form of energy beyond the violet end of the spectrum was demonstrated independently by Ritter and by Wollaston (1802). They showed that the decomposition of silver chloride (which occurs in the visible range as shown by Scheele in 1777) proceeded even more rapidly in the invisible region.

It was soon noted that both the heating effects of the infrared region and the chemical activity of the ultraviolet region are due to radiations of the same general nature as those producing visible light. Thomas Young showed the energy in the ultraviolet to be of wave nature by obtaining records on silver chloride paper of interference rings produced in this region. Phenomena of diffraction and interference were demonstrated in the infrared by Fizeau and Foucault in 1847. The occurrence of Fraunhofer lines in the infrared region of the sun's spectrum was demonstrated by Herschel in 1840; Becquerel photographed them in the ultraviolet region.

In 1860, James Clerk Maxwell laid the foundations of the modern theory of all these radiations by relating the mathematical theories of Green, Stokes and Kelvin, for wave motion as a generalized process, to the experimental demonstrations by Faraday of the electromagnetic fields set up by the motion of electric charges. He showed on theoretical grounds that electromagnetic waves should travel with the velocity of light and indicated that all these forms of radiant energy consist of such waves.

Fitzgerald showed in 1883 that a coil carrying a rapidly alternating current should radiate waves into the surrounding space. About 1886, Hertz produced these waves by means of an oscillatory discharge across a gap. He also developed methods for detecting and measuring the wave lengths of these electromagnetic waves, which can be greatly varied, and showed that they can be reflected and refracted like light. Within a few years, Marconi employed them in wireless signaling.

Radio waves are millions or billions of times longer in wave-length than are those of visible light. The waves produced by Hertz were much shorter in wave-length than those employed in radio transmission. Recently, by a refinement of the method employed by Hertz it has been possible to obtain waves having lengths of only 0.1 to 0.2 mm.[7] These are shorter than the longest infrared rays from the mercury-vapor lamp (0.4 mm.) or the Welsbach burner (0.6 mm.) as measured by Rubens. The wave-length regions of the Hertzian and infrared waves thus overlap and there is no fundamental distinction between these forms of radiant energy. The only reason for applying different names is to emphasize the experimental techniques employed for their production.

RADIATIONS BEYOND THE VIOLET

In studying the ultraviolet region the same methods of resolution employed in the visible, the prism or the diffraction grating, have been used. For detection of the radiant energy, a photographic plate usually serves. If one passes progressively toward the short wave-lengths, the study of the ultraviolet begins with a minimum of difficulty. But as one advances into the shorter wave-lengths the difficulties increase. At about wave-length 3400A, glass becomes so strongly absorbing that it is no longer of service and must be replaced by quartz or some similar crystalline substance. At about 2900A, the solar spectrum ends, due to absorption by ozone in the higher levels of the earth's atmosphere. By the use of artificial sources, such as the metallic arc, the short wave-lengths may be supplied in satisfactory intensity. It is comparatively easy to photograph and measure wave-lengths as short as 1850A, this limit having been reached by Cornu. From this point the difficulties increase very greatly as quartz becomes strongly absorbing and the gelatin of the photographic plates becomes so opaque that the radiation does not penetrate it and so can no longer act upon the silver salt. Finally, with still shorter waves, air itself ceases to be transparent, all radiations being absorbed in a very small thickness. Schumann, working between 1890 and 1903, overcame these difficulties by replacing the quartz by fluorite, by placing the apparatus in a vacuum and by making photographic plates with emulsions containing a minimum of gelatin.[8] By the methods of Schumann it was possible to obtain the spectrum of hydrogen to 1200A, at which point fluorite ceases to be transparent. Schneider[9] has suggested that lithium fluoride may be employed in place of fluorite.

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[7] Nichols, E. F., and Tear, J. D., *Proc. Nat. Acad Sci.*, **9**, 211 (1923).

Schumann did not actually measure the wave-lengths but only estimated them by means of an extrapolation of the dispersion formula for fluorite. Particularly active among more recent workers in the Schumann region have been Leon and Eugene Bloch[10] who studied many lines of manganese, chromium, silver, gold and platinum sparks of wave-length between 1869 and 1330A.

For working further into the ultraviolet, the concave grating is employed as the resolving medium; as in the visible range, it has the advantage of giving directly the lengths of the waves. The grating, usually of about one meter radius, is placed[11] in a container maintained at a very high vacuum. As, however, the gas pressure surrounding the spark which serves as the source of light cannot be too low, matters must be so arranged that the gas surrounding and carrying the discharge is not allowed to enter into the body of the spectrograph. This is done by separating the source from the rest of the apparatus by a short and narrow slit and applying a powerful mercury diffusion pump at a point just beyond this slit. With this arrangement, Lyman succeeded in determining the lengths of the waves studied by Schumann; in addition to this, he extended the optical spectra to 510A in the case of helium.

Millikan, Bowen and collaborators, as well as Edlén[12] and others, have subsequently measured lines (emitted by hot sparks) as short as 40.28A in the case of the stripped carbon atom. The existence of much shorter radiations than these had, however, been known since the discovery of x rays by Röntgen in 1895 and of gamma-rays by Villard in 1900. X-rays have wave-lengths of the order of molecular dimensions or less. Laue, in 1912, conceived the idea that the natural strata of a crystal might serve as a diffraction grating for such short wave-lengths, since the distance between the rulings would be that separating the rows of atoms in the crystal. On sending a bundle of x-rays through a suitable crystal the expected phenomenon of diffraction appeared. A short time later, Bragg attacked the problem by studying the reflection from a crystal face and succeeded in measuring x-ray wave-lengths.

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[8] Directions for making these plates are given by Hopfield, J J., and Appleyard, E. T. S., *J Opt Soc. Am*, **22,** 488 (1932)

[9] Schneider, E G, *J Opt Soc Am*, **27,** 72 (1937).

[10] Bloch, L. and E, *J Phys Radium*, **6,** 154 (1925)

[11] Lyman, T, *J. Frank Inst.*, **201,** 556 (1926), *Astrophys J*, **60,** 1 (1924); Wood, R. W., and Lyman, T, *Phil Mag.*, **2,** 310 (1926)

[12] Edlén, B., *Nature*, **127,** 405 (1931).

The characteristic x-rays of the elements range from 22A for the K-absorption edge of uranium to 0.107A. The longest x-rays measured by the Bragg crystal diffraction method are 21.53A, for one of the lines of chromium.[13] Compton[14] and also Thibaut[15] have shown that ruled gratings of the kind used for measuring the wave-lengths of ordinary light can be employed to demonstrate the diffraction of x-rays striking the grating at very small grazing incidence. This method has been much employed in studying the region between the x-rays and the shortest ultraviolet rays.

Recent absorption measurements in the Schumann region show that many common compounds absorb these ultraviolet rays and suffer decomposition thereby. The photochemistry of this region seems destined to provide many important observations.

The physicist has made considerable progress in exploring the region of wave-lengths somewhat longer than the usual x-rays by estimating the wave-lengths by the indirect method of resonance potentials. The usual method of x-ray generation is by the bombardment of a metal target with high-speed cathode rays. A modification permits the generation of radiations within the longer wave-length range. The substance which is to emit the rays is bombarded by a stream of thermionically-produced electrons moving at lower velocities produced by accelerating them by definite alterable electrical potential differences. The energy which the bombarding electrons can give to the atoms bombarded is thus known and may be expressed as the product of the charge of the electron and the potential gradient in volts per centimeter. The energy is in this way stated in units called electron-volts. Since the charge on the electron is constant, the energy is sometimes expressed less accurately as volts, for brevity. As the acceleration of the electrons is gradually increased by raising the potential difference between a plate and a charged grid through which the electrons pass, the energy possessed by the electrons becomes great enough to enable them, on striking atoms in the gaseous space through which they pass, to excite the atoms to emit radiation. Certain critical energies (in electron-volts) are necessary for this to occur. The critical voltages are obtained in such experiments by finding certain discontinuities in the current carried by the electron stream as the charge on the grid is progressively changed. At 4.9 volts, in the case of mercury vapor as the emitting atom, a single line with a wave-length of 2537A appears. This is called the mercury resonance line. At 6.7 volts, one with a wave-length of 1844A flashes out. The frequencies corresponding to the emitted wave-lengths are calculated by dividing the energy by a fundamental constant of nature, the quantum of action or Planck's constant, the nature of which will be discussed in the next chapter.

The method has been extended to the region of wave-lengths only slightly longer than x-rays. The emission of radiations in such experiments is made evident by a sudden increase of gaseous ionization or of photoelectric effect as the accelerating voltages are gradually raised beyond the critical values. Holweck[16] has shown that a continuous radiation is produced when accelerating voltages between 25 volts (500A) and 280 volts (44A) are employed. He used an apparatus consisting of a sort of Coolidge x-ray tube made entirely of metal in which the cathode and anode are separated by a distance of one millimeter. The tube is operated at potentials of 25 to 1800 volts. As the rays emerge from the tube through celluloid films of a thickness of 0.00005 mm., they enter an ionization chamber. Superposed on the continuous spectrum there is a line spectrum characteristic of the element used as a target.

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[13] Thoraeus, R., *Phil. Mag.*, **1**, 312 (1926).

[14] Compton, A. H., *Proc. Nat Acad. Sci*, **11**, 598 (1925).

[15] Thibaut, J., *Compt. rend.*, **182**, 55, 1141 (1926); **185**, 62 (1927); *J. Phys. Radium*, **8**, 13 (1927); *Nature*, **121**, 321 (1928); *Physik. Z.*, **29**, 241 (1928); *J. Opt. Soc Am*, **17**, 145 (1928); De Broglie, *Compt. rend.*, **190**, 93 (1930)

[16] Holweck, F., *Compt. rend.*, **173**, 709 (1921); *J. Chim. Phys.*, **22**, 311 (1925)

These radiations lack penetrating power; this is the reason why it is necessary to use the thin celluloid window. They are said to be soft x-rays. The term hardness connotes penetrating power. Soft x-rays (but not as soft as those of Holweck) have been used by Günther[17] in the examination of thin layers of biological products such as leaves or the wings of insects. These rays, which because of their greater ease of absorption, are better suited than hard x-rays for the treatment of skin diseases, are produced in tubes operated at voltages low (4 to 12 kilovolts) compared with those used for more penetrating x-rays. Egress is through a window of a special glass in which sodium, calcium and silicon have been replaced by lithium, beryllium and boron.

As the wave-lengths increase from the x-ray to the ultraviolet region, the absorption of the radiations by many substances increases to a maximum beyond which there is a diminution in absorption as the better-known regions of the ultraviolet are reached. Holweck found that 0.00027 mm. of celluloid, which has a relatively low absorption in comparison with other substances in this region, transmits only 3 per cent of the radiation of wave-length 310A at which it has its maximum absorption.

The gamma-rays produced by radioactive decay, as measured by Ellis, have wave-lengths between 0.26 and 0.005A. Very penetrating radiations known as cosmic rays, discovered by Wulf and by Gockel between 1909 and 1914[18] have recently been the subject of particularly extensive investigation by Kolhörster, Regener, Millikan, Compton, and many others Although some workers consider them as electromagnetic waves of extremely high frequency, most believe them to be some type of high velocity movement of minute corpuscles. They are certainly non-homogeneous, the highest frequency band has so enormous a penetrating power that it passes through 200 feet of water or 18 feet of lead before being completely absorbed, although two or three inches of lead absorb the hardest gamma-rays.

The Electromagnetic Spectrum as a Whole

The radiations from wireless telegraph waves to gamma-rays which make up the electromagnetic spectrum are summarized graphically in Figure 1. The range of wave-lengths is so great that a logarithmic scale is required. A doubling of the wave-length is called an octave, a familiar term in music. The diagram of the electromagnetic radiations covers about sixty octaves, and of these, only one represents the radiations which are visible. In certain regions, as between the Hertzian and the infrared regions, an overlapping of the radiation known by various names, is indicated. This means merely that radiations of wave-lengths included in the region of overlapping have been produced by the methods which are usually employed for the production of wave-lengths on both sides of this region. A consideration of the mechanisms by which radiations are produced indicates that the nature of the oscillator bearing the charge, whether it be a coil of wire, a molecule moving as a whole, valence electrons in a molecule or atom, or nuclear electrons, usually determines, although in a very indirect manner, the wave-length of the radiations produced.

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[17] Günther, P, *Z. Angew Chem.*, **44**, 404 (1931).

[18] Compton, A. H, *Nature*, **135**, 695 (1935). The existence of a shortest possible wave-length of 6.2×10^{-6}A has been assumed by A. March, *Z. Physik*, **108**, 128 (1937).

It is the wave-length which serves to characterize the nature of a radiation and to indicate its penetrability, chemical and optical properties and utility. The amplitude of the wave (or more accurately, the square of the amplitude) serves to visualize the intensity of the radiation.

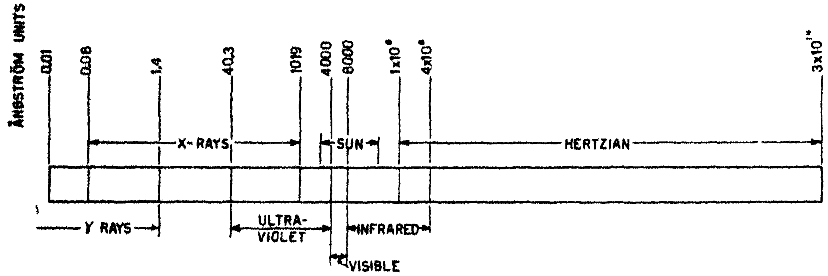

FIGURE 1. Electromagnetic Spectrum.

The impression has been given in the preceding discussion that the wave theory offers an adequate expression of the behavior of radiant energy. It must now be pointed out that there are a considerable number of effects, particularly those concerned with the mechanism of the emission and absorption of radiant energy, for which the wave theory has no ready explanation. These effects are better comprehended on the basis of the quantum theory, according to which quanta or "bundles of energy" are emitted from the source, as explained in the following chapter. The quantum theory may be adequately applied over a considerable field, notably to photoelectric phenomena, Bohr's theory of the atom, and the relationship between the frequencies of lines in emission spectra. Indeed, it has served in the last few years as a great correlating principle for a wide variety of physical properties as diverse as the specific heats of elements and the absorption of radiations.

Great changes in physical theory have arisen from the recent work of De Broglie, Schrodinger and of Heisenberg Their theories have led to the creation of a new system of mechanics in which the motion of a material particle is always associated with a wave motion, the wave length of which is determined by dividing Planck's universal constant by the momentum of the moving particle. Conversely, in the words of Planck, radiant energy traveling with the speed of light appears on interacting with matter, to "shrink together and concentrate itself at separate points which move like corpuscles, and for that reason are called light-quanta." [19] Each such quantum of radiation is now called a *photon*.

It appears from the newly established points of view that there can be neither pure corpuscular motion nor pure wave motion in physics. Rather, every corpuscular motion is attended by some measure of wave motion and every wave motion involves something of corpuscular motion. The distinction between the two is only gradual and quantitative. The acceptance of such an unlooked-for conception has followed from the experiments of Davisson and Germer[20] which, by revealing the diffraction of electrons, demonstrated the motion of even these minute particles to be such as to imply a wave-nature for them.

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[19] Planck, M., *J. Frank. Inst.*, May 18, July 15, 1927.

On the other hand, the elementary quantum plays no part in the equations of Maxwell for radiant energy, which have not been invalidated in even the finest interference measurements. At present, therefore, physicists and photochemists employ both the wave and the quantum aspects of radiant energy in interpreting their data. Wave-lengths or frequencies are used to designate the quality of a radiation, but in discussing its photochemical effects quantum concepts are necessary.

[20] Davisson, C., and Germer, L. H., *Phys. Rev.*, **30**, 705 (1927); Thomson, G. P., *Proc. Roy. Soc.*, **A117**, 600 (1928).

Part I

The Sources of Ultraviolet Radiations

Chapter 2

Mechanism of the Emission of Radiant Energy

The occurrence of a photochemical reaction in the ultraviolet region presupposes the absorption of ultraviolet radiation. An understanding of the mechanism of the reaction involves a knowledge of the processes by which the radiant energy is absorbed by one or more of the reacting substances. Since the time of Kirchhoff it has been realized that absorption of radiant energy is the converse of the process by which it is emitted. Reference to this has been made in the preceding chapter in the discussion of the well-known Fraunhofer dark lines in the spectrum of the sun. Since our present views regarding the interaction of radiant energy and matter were derived chiefly from studies of the manner in which matter emits radiations, it seems logical to describe the emission mechanism of the ultraviolet sources in common use before proceeding to a consideration of the absorption of radiations by substances concerned in chemical reactions.

Illuminating sources consist of some form of matter heated to incandescence, such as the carbon particles in an oil lamp or the luminous flame of a gas burner, glowing calcium oxide in the old limelight, rare-earth oxides in the Welsbach gas mantle, or electrically heated wires glowing in an atmosphere of inert gas. When, as in the first of these, the temperature is relatively low, the color of the rays emitted is a mixture of red and yellow. Sources at higher temperatures emit increasing quantities of blue rays so that the color of the light appears more nearly white. At still higher temperatures increasing amounts of the shorter ultraviolet rays appear.

In 1869, Stefan showed that the total amount of energy emitted by a black body increases as the fourth power of its temperature Although the term "black body" refers to an idealized concept like that of a perfect gas, Stefan's law applies as an approximation to many substances. In experimental work, it may be approximated by a hollow sphere raised to a suitable temperature. The radiation emerging from a small hole is dispersed by a prism or grating and the intensities of the radiations in the various spectral regions are measured by a thermopile and galvanometer. Data of this sort are shown by the curves of Figure 2 in which the abscissae represent wave-lengths and the ordinates intensities in arbitrary units. Curves for three temperatures are included. They rise with increasing temperature in accordance with the Stefan-Boltzmann law; the areas beneath the curves vary as the fourth power of the temperature.

It may also be noted that as the temperature is increased, the wave-length of the maximum intensity shifts from the infrared region to the visible range. The red just begins to show at a temperature of approximately 1500°Abs. and the maximum lies at approximately 20000A. At the temperature of the tungsten lamp (2000°Abs.), the maximum is at 15000A. At solar temperatures (approximately 6000°Abs.), it is in the green region, a considerable proportion of ultraviolet rays also being emitted. Wien's displacement law states that with rising temperature the emission shifts to higher frequencies.

After the establishment of these two laws of radiation, physicists sought a theoretical explanation of the manner in which an increase in the temperature of a substance might cause it to emit electromagnetic waves. Since such waves in the Hertzian region are known to be produced by the oscillation of an electrical charge, it appeared necessary to conceive of some type of charged oscillator either borne by or located within the atoms of the solid which emits radiations. Mathematical physicists, notably Lord Rayleigh, Maxwell, and Jeans, attempted to develop a theory for the distribution of energy emitted by various hypothetical oscillators, with frequencies dependent upon the temperature. However, these attempts all led to the conclusion that when radiant energy is in equilibrium with matter, the total amount of radiant energy per unit volume should be infinite and that most of it should lie in the short-wave region of the spectrum. Actually, the laws of Stefan and Wien show that but a finite amount of radiant energy can be in equilibrium with matter at a given temperature, and that only at high temperatures does much of it lie within the ultraviolet.

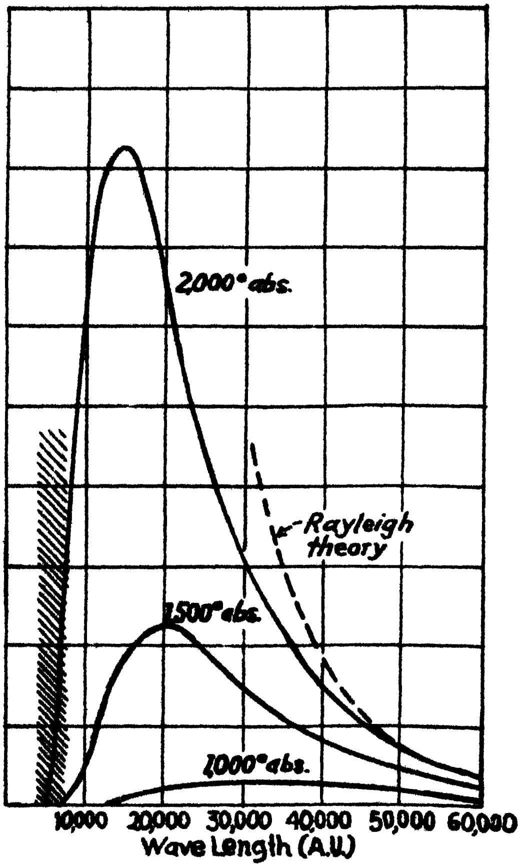

FIGURE 2.

Influence of Temperature on Blackbody Radiation (Eldridge, "Physical Basis of Things," New York, McGraw-Hill Book Co.).

This impasse was overcome by Planck,[1] who in 1900, advanced a theory of radiation in which the motion of hypothetical oscillators could be made to account for the radiation of energy in the amounts and wave-length distribution required by the laws of Stefan and Wien. Its acceptance was delayed because, in his derivation, Planck had been obliged to make certain assumptions at variance with the dynamics based upon Newton's laws of motion. The assumption was made that the energy of a vibrator in the heated body is increased only by jumps as the temperature is increased. These discontinuous increments of energy were called quanta and led to the name of quantum theory for the new viewpoint.

The investigations of Einstein[2] on the photoelectric effect did much to secure acceptance for the quantum theory, since they demonstrated the existence of discontinuities in the interaction of matter and radiant energy. Additional justification for the adoption of the radical concept of a discontinuity in the energies associated with matter in motion came in 1912 from a field of physics at first sight far from that of radiation when Debye[3] successfully applied the quantum theory to the study of the specific heat of solids. Perhaps the greatest factor which contributed to the present general acceptance of the quantum theory was the success of the work of Bohr on the interpretation of spectra, which was founded upon that theory.

It is the purpose of this chapter to acquaint the chemist who may be untrained in modern physics with that minimum of the newer viewpoint necessary for an understanding of the characteristics of the useful sources of ultraviolet radiations.

To that end, it is necessary first to inquire into the meaning of Planck's assumption. His idea implies that a physical system can exist in only certain discrete energy states. On the acquisition of energy, a system jumps from one to another of these states without passing through a continuous series of intermediate ones. A rotating dumbbell possessing a definite angular momentum can acquire energy and assume a new state of more rapid rotation with greater angular momentum. It is usual to think of it doing so by speeding up through all intermediate speeds of rotation. The quantum theory, however, makes the radical assumption that this is not the case and that, in speeding up, the change in rotational energy is discontinuous. Only certain rotational energies can be possessed by the dumbbell, and when speeding up, it can jump only from one to another of these. At first sight this seems contrary to everyday observation This is not, however, necessarily the case because the energies possessed by a large object in the permissible states differ so little that the speeding-up process appears to be continuous. Matters are quite different in the case of minute systems such as those of atoms or electrons where the discontinuity of the process dominates the picture. Poincaré has shown mathematically that the fact that the total radiation from a black body at a finite temperature is finite requires that the ultimate motion involved in the mechanism of radiation be in some way discontinuous.

Since the work of Planck, different, and in some respects more satisfactory, derivations of the quantum laws of radiations have been given by Jeans,[4] by Darwin and Fowler,[5] and by Einstein.[6] The last of these, which has led to one of the fundamental laws of photochemistry, requires that the molecules emitting radiations can exist only in certain definite energy states, and that when a molecule jumps from one state to another the accompanying loss or gain of energy is always one or more complete quanta of radiation, fractions of a photon not being emitted or absorbed.

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[1] Planck, M , *Ann. Physik* , **4,** 553 (1901).

[2] Einstein, A , *Ann. Physik* , **20,** 199 (1906)

[3] Debye, P., *Ann Physik* , **39,** 789 (1912).

[4] Jeans, Sir J , *Phil. Mag.*, **20,** 953 (1919).

[5] Darwin, C. G., and Fowler, R. H., *Phil Mag* , **44,** 450 (1922).

[6] Einstein, A., *Physik. Z.*, **18,** 121 (1917).

It is as meaningless to speak of the amount of energy in a quantum without specifying its frequency as it would be for a chemist to speak of the weight of an atom without stating to which element he referred. The magnitude of a quantum of radiation depends upon the wave-length (frequency) of the radiation. The relation between the masses of the atoms of different elements is a complex one, but that between the magnitudes of the quanta of radiations of various frequencies is the very simple one of direct proportionality. The frequency of the radiation multiplied by a constant gives the energy per quantum of that radiation. In most physical literature the frequency is denoted by the Greek letter ν and the constant by h. Therefore, the energy ϵ of a photon of radiation of a given frequency ν is given by

$$\epsilon = h\nu$$

This means that the constant h can be expressed by $h = \epsilon \times \frac{1}{\nu}$, that is, energy multiplied by the reciprocal of a frequency, which is the period or time of a vibration. The unit in terms of which h is measured is then one of energy multiplied by time, or erg seconds. The value of h has been determined by many methods to be 6.55×10^{27} erg sec. The erg second is called by physicists a unit of action, this term being used to denote the product of energy and time.

When the quantum constant h is multiplied by the very large number which expresses the frequency of green light, the resulting energy is found to be still a small number, 3.93×10^{12} erg. This is nevertheless of such an order of magnitude that its effects in producing discontinuities in radiation are discernible by physical methods. The quantum of energy associated with a line at 5890A would be 1.6×10^{-16} erg greater than that associated with one at 5891A.

CONTINUOUS AND LINE SPECTRA

The spectrum produced when the radiation emitted by a glowing solid is passed through a prism blackens a photographic plate continuously and rather uniformly. An additional effect is produced when gases or vapors at high temperatures emit light. In 1829, Sir John Herschel examined the spectra of the colored light produced by heating certain salts in an alcohol flame and found the emitted energy to appear concentrated in lines corresponding to relatively few wave-lengths. Such spectra are called line spectra, or discontinuous spectra. The wave lengths at which such lines occur characterize the elements the vapors of which produce them when heated. Bunsen and Kirchhoff employed these bright-line spectra in the detection of those elements which emit lines under these conditions. In the preceding chapter, it was noted that the Fraunhofer black lines which cross the spectrum of sunlight are due to the absorption of certain lines by elements present in gaseous form in a layer surrounding the sun. The positions of these black lines on the wave length scale correspond to the positions of the bright lines emitted by the same elements when heated and viewed directly. The identification of the Fraunhofer lines with those emitted by elements in the laboratory provided the means by which it became possible to determine which elements are present in the reversing or absorbing layer of gas surrounding the sun.

The bright line emission spectra of the elements consist, when viewed through a spectrograph, of a series of lines separated by regions of comparative darkness. They are produced as the result of processes occurring in widely separated atoms or molecules of substances in the vapor or gaseous state. The same processes occur also in the atoms or molecules comprising incandescent solids, but in this case any natural frequencies of rotation or vibration associated with these atoms or molecules are masked by effects produced by the continuous bombardment of neighboring atoms or molecules. The result is that the spectrum is continuous and yields no information in regard to the nature of the atoms or molecules present in the incandescent solid. As indicated in Figure 2, the predominating frequency is, instead, a function of the temperature. Some exceptions to this statement may be noted. The rare earths used in the Welsbach gas mantle, when heated to incandescence, emit line spectra. Nichols[7] described ten or more crests on the brightness curve of glowing neodymium oxide, which, however, bear no relation to the true line emission or absorption spectra of this compound. The theory of the origin of this type of spectrum has recently been discussed by Van Vleck.[8] Grain size influences the nature of the temperature radiation from other metallic oxides.[9]

Just as certain incandescent solids give indications of line spectra superposed on their continuous radiation, so conversely gases or vapors produce beneath their characteristic line spectra a more or less faint continuous background. Its origin has been attributed to the effects of free electrons of varying kinetic energies joining with ions to produce atoms or, in the case of molecules, to recombination of free atoms possessing varying kinetic energies. (See Chapter 9.)

There are two kinds of line spectra, those emitted by atoms and those emitted by diatomic or polyatomic molecules. The latter spectra, *i.e.*, molecular spectra, were called band spectra by the earlier spectroscopists whose apparatus of low resolving power revealed them only as a number of bands of light and darkness often overlapping to produce a channeled or fluted appearance. With more modern equipment they have been resolved into groups of lines. Molecular spectra will be reserved for discussion in Chapter 13; the remainder of the present chapter will be devoted to a consideration of the order underlying the positions of the lines in atomic spectra, and the theories of the mechanism of emission of radiation which have been devised to account for it.

The photochemist needs to know something of the theory of line spectra for two reasons. In the first place, his sources of radiation are predominantly means for treating gases or vapors of elements so that they emit line spectra. (In most sources the line spectra are somewhat complicated by the incidental production of some molecular spectra.) The lines which carry the radiant energy are at first sight spaced quite at random, and the intensities of different lines vary greatly in an apparently irregular manner. If it is desired to carry out a reaction by energy of wave-lengths between 2500 and 2600A, it is necessary to know which sources emit line spectra having strong lines located within this region. If, on the other hand, one wishes to test the action of the region of 2800-2900A, a source must be chosen having strong lines in that region, and only faint ones, if any, in the 2500-2600A region.

In the second place, the photochemist must understand the process by which molecules absorb energy. Since this is the converse of the process by which they emit molecular spectra and is quite complicated, it may best be approached after

[7] Nichols, E. L., *Proc. Nat. Acad. Sci.*, **11,** 47 (1925); *Chem. Abs.*, **19,** 1376 (1925).

[8] Van Vleck, J. H., *J. Phys. Chem.*, **41,** 67 (1937).

[9] Liebmann, G., *Z. Physik*, **63,** 404 (1930); Skaupy, F., *Physik. Z.*, **28,** 842 (1927).

the principles regarding the emission of atomic spectra are understood. Furthermore, the theory of atomic spectra itself represents one of the most important contributions which the students of the physics of ultraviolet radiations have made to chemistry, for it was the work of the spectroscopist which laid the foundation upon which have been erected the present theories of atomic structure.

Classification of the Lines in Atomic Spectra into Series

The spectrum of hydrogen, as obtained in a Geissler tube, consists of comparatively few lines. One is red, one blue, two are violet and many lie in the ultraviolet region. (Figure 3) They are spaced far apart in the visible and approach each other more closely as the region of higher frequencies is approached. They occur at 6563, 4861, 4340, 4102, 3970, 3889, and 3825Å. About 31 of these lines are recognized, piling up more closely to each other to reach a limit at 3646Å. These lines are called the Balmer series after the scientist who showed in 1885 that the frequencies of the first nine lines could be expressed by a simple mathematical equation implying an underlying regularity.

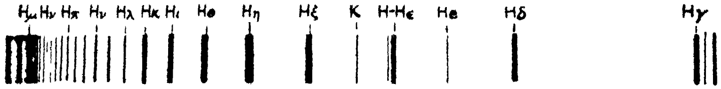

Figure 3. Balmer Series. (Eldridge, "Physical Basis of Things," New York, McGraw-Hill Book Co)

Rydberg employed a more general expression which in a modified form applies to many elements. In the simplified form applicable only to hydrogen, it is

$$\nu = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where n_1 and n_2 are integers n_2 being the larger, ν is the frequency of one line in the hydrogen spectrum, and R is a constant. By letting R be 109,737, n_1 be 2 and n_2 be successively 3, 4, 5, etc , the successive values of ν given by this expression correspond to the observed frequencies of the spectral lines of Balmer, expressed in wave numbers It is to be noted that the wave-number (or frequency divided by 3×10^{10}) is given by this expression as the difference between two terms. If the second term is nearly as large as the first, as when n_2 is only one unit greater than n_1, the difference between the two terms or the frequency of the line, is small, and the line lies in the red region Since n_2 is in the denominator, an increase in its value will lower the value of the second term, making its difference from the first term greater and thereby increasing the frequency of the corresponding line. Successive increments of n_2 increase the frequencies of the corresponding lines by progressively smaller amounts. When n_2 becomes infinitely great, the second term disappears and the expression reduces to the frequency of the first term. This is, therefore, the limit of the series.

If, now, the calculation is repeated, this time starting with 3 for n_1 and 4, 5, 6, etc. for n_2, a new series of frequencies approaching a different limit will be obtained. The frequencies are such that these lines fall in the infrared region. This series of lines was discovered by Paschen in 1896. By starting with 4 for n_1 still another series of lines can be obtained; its limit lies still farther out in the infrared. Lines of this series were discovered by Brackett in 1922. When n_1 is made equal to one, the equation yields a series of lines in the ultraviolet. Most lie far out in the difficultly accessible region; they were discovered by Lyman.

THEORY OF THE MECHANISM OF THE EMISSION OF LINE SPECTRA

The Hydrogen Spectrum. The fact that the frequency of a spectral line is related to the difference between two terms was long a source of difficulty to the theorists who conceived of the spectral frequencies as in some manner related to natural frequencies of intra-atomic vibrations. The spectra of more than twenty elements had been resolved, at least in part, into series when Bohr in 1913 successfully employed the quantum theory of Planck in accounting for the origin of the lines in series spectra of the elements. He applied the new and almost unaccepted idea of the discontinuity of "action" to the dynamics of the structure of the atom as pictured by Lord Rutherford. In Rutherford's theory an atom is composed of a central positively charged nucleus around which there revolve in closed orbits as many electrons as are required to balance the positive charge of the nucleus. The positive charge of the nucleus as well as the number of electrons is equal to the atomic number of the element. The hydrogen atom consists of one electron revolving around a nucleus of equal and opposite charge. In helium, there are two revolving electrons, in lithium three, in carbon six, and so on to uranium with 92 electrons.

Although the orbits of the electrons are conceived as elliptical, it is perhaps simpler to regard them as circular in an introductory consideration of the theory as it applies to hydrogen. The electrostatic force of attraction between the electron and the oppositely charged nucleus balances the centrifugal force of rotation of the electron and so holds it in its orbit. A difficulty arises when the radiation of energy by such a system is considered. Motion in a circle is accelerated motion. It is fundamental in electrodynamics that an accelerated charge radiates energy, and the electron would be expected to spiral in gradually toward the nucleus. Actually, however, the spectroscopist knows that an atom emits no measurable radiation unless energy is supplied to it in some manner as by mechanical impact, by heat or by an electrical discharge.

The discrepancy between the experimental results and those expected on the basis of electrodynamics was as serious as that encountered in the study of black body radiation, which Planck had met by making the radical assumptions of the quantum theory. Bohr met the difficulty in the same manner by adopting the theory of Planck. He assumed it possible for the electron of the hydrogen atom to revolve, without radiating energy, in certain discrete orbits in which its angular momentum mvr (m is the mass of the electron, v its angular velocity, and r the radius of the orbit) is an integral multiple of $h/2\pi$, that is, $nh/2\pi$. By using known values of the mass and charge of the electron, it was possible to calculate from this quantum condition and an equation relating the centrifugal force and the electrostatic force between the electron and the nucleus, the radii of the orbits in which the electron could move without radiating energy. These were found to have radii of 0.5, 2.0, 4.5 and 8Å, when n, called the quantum number, had the successive values 1, 2, 3 and 4. The radii of the permitted orbits increase as the squares of the quantum numbers. Each such orbit represents a state in which the hydrogen atom possesses a calculable amount of energy. Thus the atom may exist in definite energy states, or may be said to possess definite energy levels.

Bohr assumed that energy is radiated only during the time in which the electron falls from an orbit in which the atom has greater energy to one in which it has lesser energy; that is from an outer to an inner orbit. The energy emitted is the difference between the energies possessed by the atom in the initial and final states. The transition may be either between adjacent or more widely separated permissible orbits or energy states. In terms of the quantum thory, the energy radiated is expressed by $h\nu$. Therefore, the difference between the energies in the initial and final states when divided by h yields the frequency of the line emitted.

It appears, therefore, that in the Bohr theory the frequency of the emitted line is not directly related to that of any vibration in the atom before or after emission, but to a difference between the energies possessed by the atom before and after emission. Emission from an atom persists for but a very brief period. The persistence of the lines seen to be emitted from a discharge tube is due to the successive emissions of the line by different ones of the great number of atoms in the tube. Of these, some at a given moment are in the resting state, others are being excited by the electrical discharge as a preliminary to emission, others are in the excited state in which the atom holds the energy acquired during excitation, and still others are emitting the observed line. Bohr's theory affords an explanation of the fact that in the Rydberg formula the wave-number of the emitted line is represented as the difference between two terms.

In terms of this theory, the various sources of ultraviolet light are devices for introducing energy into atoms (or sometimes molecules) in order to raise them to higher energy levels. This process is called excitation. In the Bohr picture, this consists of shifting an electron from an inner orbit, in which its potential energy has the greatest negative value, to an orbit of greater radius. The excited atoms have but a very transient existence, usually of the order of 10^{-8} second, after which the electron drops to an orbit of lower energy, which may or may not be the innermost orbit. It is during this process that a spectral line is emitted.

A transition of an electron from the second to the first energy level is accompanied by the emission of the first line of the Lyman series of hydrogen lines in the ultraviolet. An atom in which the electron transition is from the third to the first energy level emits the second line, one from the fourth to the first level emits the third line, and so on. The differences in energy in the successive energy levels lessen as n becomes large. Therefore, the differences between these higher levels and the resting level differ less and less as n becomes large and the successive lines of higher frequency occur closer together as the limit for infinite n is approached.

It is by no means always the case that the electrons fall back from higher levels to the resting level or innermost orbit. When they fall back only to the second level, the lines of the Balmer series are produced. Transitions to the third level gives the lines of the Paschen series. These statements follow directly from the Rydberg formula, the number used for n_1 giving the orbit to which the electrons drop during emission.

It may not be apparent why thirty or more lines of the Balmer series are seen simultaneously in the emission from a discharge tube. In any source there is present a tremendous number of atoms, some moving with high and some with low velocities, and others at rest. When such a mass of atoms is excited by the passage of an electrical discharge, there are differences in the states of excitation attained by different atoms. Some are excited to the second, and others to various other energy levels, even very high ones. Each atom then emits in a manner depending upon its state of excitation. When the radiation from the whole collection of emitting atoms is viewed through a prism, the lines resulting from each of the many types of transition in progress in different atoms are seen simultaneously. The relative intensities of the lines are related to the probabilities with which the excited states giving rise to the lines are produced under the experimental conditions of excitation.

Elements Other Than Hydrogen. In the case of other elements, the line spectra are much more complex. In the iron spectrum, there are thousands of finely spaced lines. King[10] has recorded more than 3000 lines in the cerium spectrum, 1600 of which lie between 3000 and 4700A.

In the case of the spectra of the alkalies, it was found possible to classify the lines, at first by their distinctive appearances, into four series. Three of these were named by Rydberg the principal, sharp and diffuse series. A fourth series, discovered by Bergman in the infrared region, was called by Hicks the fundamental series, for reasons no longer pertinent. The descriptive significance of these names is not maintained in the case of more complex elements but because of their historical significance they have been generally retained and their abbreviations, P, S, D and F, are in common use in the designation of spectral terms.

The Rydberg formula for the frequencies of the lines of a series for the alkalies differs from the simplified form applicable to hydrogen in having two additional constants, μ_1 and μ_2:

$$\nu = R\left(\frac{1}{(n_1+\mu_1)^2} - \frac{1}{(n_2+\mu_2)^2}\right)$$

These constants have fractional values characteristic of the elements. These differ also for lines of the sharp, principal, diffuse and fundamental series of a given element. In the case of sodium, when μ_1 is 0.626 and μ_2 is 0.13, the expression, using $n_1 = 1$, gives the lines of the principal series. If n_1 is taken as 2 and the μ_1 and μ_2 values are reversed, the lines of the sharp series are given. By replacing μ_2 by a new constant, $\mu_3 = 0.99$, in the second term, the lines of the diffuse series are obtained. By making $\mu_1 = 3$, using μ_3 in the first term and still another constant $\mu_4 = 0.999$ in the second term, the infrared lines of the Bergman or fundamental series are found. These four constants, known also as "defects," are only approximations, and the lines are never given as exactly as is the case with the simplified expression for hydrogen in which "defects" may be neglected in all but the most accurate work.

The existence of these "defects" and the resulting occurrence of lines of sharp, diffuse, principal and other series, implies that the energy states of the alkali atoms cannot be sufficiently characterized by the single quantum number n. A second number L is required to distinguish the energy levels which exist. In the earlier development of the theory it was assumed that this was due to the fact that the orbits were elliptical rather than circular. Electrons moving in such orbits would have, in addition to a rotary motion about the focus at which the nucleus is situated, a radial motion toward and from the nucleus. For each of these forms of periodic motion quantized energy states were postulated. This increased the number of energy levels, since for each n value there may be several L values. In general, the energy differences between L states with the same n value are less than those between the states with successive n values. It has been found that L, called the orbital quantum number, may have the value zero, or any integer up to one less than the value of n.* An energy level or term for which L is zero is an S term, one for which it is 1 a P term, one for which it is 2 a D term, and one for which it is 3 an F term.

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[10] King, A. S., *Phys. Rev.*, **29**, 366 (1927).

* It is unnecessary to discuss in detail the history of the development of the theory of these quantum numbers or of others since introduced. They were first arrived at by an extension of the Bohr theory by Sommerfeld, but have subsequently been found to emerge naturally from the theories of quantum mechanics.

As in the case of the Bohr theory of the hydrogen atom, the spectral lines result from transitions from higher to lower energy levels. Not all of the theoretically possible transitions between terms are found to occur under the usual experimental conditions, or, as the spectroscopist would express it, not all terms combine to give lines. It has been found possible to predict which transitions may occur by the aid of certain *selection rules*. These were originally obtained empirically, but have since been found to have a theoretical basis. One selection rule states that, in absorption or emission, L must increase or decrease by one. In other words, transitions may occur only between states whose L values differ by but one unit. S states can undergo transitions only to or from P states, but P states may combine with either S or D states, D states with P or F states, and so on. Other transitions are said to be forbidden. Selection rules are not, however, absolutely binding, since under certain conditions, lines corresponding to transitions other than those given by the rules may appear with low intensities. Thus, the term *forbidden* is a misnomer, since forbidden lines are really lines corresponding to transitions of only low probability. The quantum mechanics affords methods for calculating the probability of transitions.

There is no selection rule limiting the number of integers by which the principal quantum number *n* may change in a transition.

Spectroscopists denote a spectral line by writing the terms separated by a dash. In writing the terms the abbreviations S, P, D, etc. are used to indicate the L value of each; these are preceded by numerals for the *n* value of each. Thus a line of the principal series may be written 1S-2P, or in general, 1S-*n*P, successive values of *n* giving the successive lines of the series Lines of the sharp series are given by 2P *n*S, those of the diffuse series by 2P-*n*D, of the Bergman series by 3D-*n*F. The symbol of the last term refers to the series of which the lines are members. The first term gives the limit of the series. The sharp and diffuse series of lines of the alkalies approach the same limit, depending upon whether L increases or decreases by one in falling from a state of greater to one of lesser energy.

Further complications arise when the processes of emission or absorption occur in a magnetic field. Under these conditions, a given line may be split into several lines (Zeeman effect). Even without the application of a magnetic field, certain lines of the alkalies, *e.g.*, the D line of sodium, may be observed to be resolved by a spectroscope into two closely adjacent lines, called a doublet. In the case of elements of other groups of the periodic system there may be triplets, quadruplets and even higher degrees of multiplicity, thus greatly complicating the spectra. In some cases, the corresponding lines of multiplets may not lie close together but may be hundreds of Ångstrom units apart and be separated by great numbers of intervening lines.

These effects may be accounted for by considering that the terms are split into others of but slightly different energy levels. Thus, to characterize the greater number of terms implied, a third quantum number, J, called the inner quantum number, is employed. In writing the terms, the value of J is placed as a subscript to the right, as in $1S_{1/2}$, $2P_{3/2}$, etc. The multiplicities of the terms are indicated by upper left indices, as in $^3D_2$.[11] A selection rule states that J may either increase or decrease by one, or need not change in a transition, except that in cases in which it is initially zero, it must change.

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[11] For a discussion of this notation, see Russell, H. N., Shenstone, A. G., and Turner, L. A., *Phys. Rev.*, **33**, 900 (1929).

The multiplicities exhibited by an element depend upon its position in the periodic table and must, therefore, be related to the electronic configuration of the atom. The terms of atoms with an even number of electrons have odd multiplicities. Those of atoms with an odd number of electrons have even multiplicities. Elements of the alkalies have doublets, those of the alkaline earths singlets and triplets, those of the next group doublets and quartets, and those of the next group singlets, triplets, quintets, etc.

Many attempts have been made to arrive at a physical interpretation of these features of the spectral terms by extending the Bohr theory to atoms having more than one electron. These take into account the interactions between the electrons, and involve complexities of interest chiefly to the specialist in atomic spectra.[12] It need only be mentioned here that this development showed the need of a new concept—the electron spin—introduced by Uhlenbeck and Goudsmit[13] and by Bichowsky and Urey.[14] This assumes each electron to rotate about its own axis besides moving in an orbit about the nucleus.* The electron spin has an angular momentum $1/2\, h/2\pi$.

The effects of the spins of the electrons in the atom (only the valence electrons or those outside the kernel need be considered) may be lumped together by the methods of vector analysis into a resultant spin vector S for the atom. This assumes only certain discrete values. If all the spins are parallel, S is equal to one-half the number of electrons since each contributes 1/2. The contributions of antiparallel electrons neutralize each other. For example, if as in the alkaline earths, there are two electrons outside the kernel, S will be one if the spins are parallel and 0 if they are antiparallel. The extreme values which the quantum number J may possess for a given L level for a given atom are obtained by adding L and S and by subtracting S from L. J may also have all intermediate values which differ from these extreme values and from each other by integers. This means that if L is greater than S, the number of J values for a given L (the multiplicity of the term) is given by $2S+1$.

It must now be emphasized that the Bohr theory, although useful in stimulating the earlier development of the theory of spectra, had many arbitrary features and, indeed, probably was in error in certain features. The quantum numbers and selection rules have subsequently been shown to emerge more logically from quantum mechanics. The methods employed require a degree of mathematical training possessed by relatively few chemists and must be sought in special texts. This development has arisen from the work of Heisenberg[17] on matrix mechanics and independently from the introduction by Schrödinger[18] of the wave equation of De Broglie[19] into the classic equation for the propagation of elastic waves. The result of the latter approach was a differential equation which could be applied to the motion of the electron in the hydrogen atom. This equation has a discrete set of solutions called *eigenfunctions* which represent energy states of the atom. According to these theories, the electron orbits of the atom have lost their once-assumed definiteness and it is possible only to calculate the probability of an electron being found within a definite minute volume of space. They do, however, confirm the existence of definite energy levels, transitions between which give rise to the spectral lines. Indeed, it may be said that although the Bohr theory had assumed their existence, their occurrence was nevertheless inexplicable and, until the advent of the quantum mechanics, marked a sharp break with all previous conceptions of electrodynamics.

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[12] For accounts of these see books on atomic spectra The following have been consulted in preparing this brief summary Johnson, R C, "Spectra," London, Methuen, 1928; Herzberg, G., "Atomic Spectra and Atomic Structure," New York, Prentice-Hall, 1937, White, H. L, "Introduction to Atomic Spectra," New York, McGraw-Hill, 1934, Candler, A. C, "Atomic Spectra and the Vector Model," 2 Vols, Cambridge Univ Press, 1937 An exhaustive bibliography has been given by Gibbs, R C., *Rev Modern Physics*, **4**, 278 (1932).

[13] Uhlenbeck, G F., and Goudsmit, S, *Naturwiss*, **13**, 953 (1925), *Nature*, **117**, 264 (1926); see also Compton, A H, *J. Frank. Inst*, 145, *1921*, Aug

[14] Bichowsky, F. R., and Urey, H C. *Proc Nat Acad Sci.*, **12**, 80 (1926)

* The state of each individual electron in an atom can be described by four quantum numbers, n the principal quantum number, l the orbital quantum number, m_l the magnetic quantum number, and m_s the electron spin number. n can have any integral value, l can have any integral value up to one less than n, m_l may have any integral value between l and $-l$, including zero, (or a total number of possible values equal to $2l+1$), and m_s can have only the values $-1/2$ or $+1/2$. Pauli's exclusion principle states[15] that no two electrons in the same atom can have all four quantum numbers the same. This principle and the restrictions on the values which the quantum numbers may possess permit the description of the electron configurations of the atoms of all the elements of the periodic table. Fowler states[16] that it is possible to predict from the electron configuration of an element, however complex, the main features of its spectrum.

[15] Pauli, W. Jr., *Z Physik*, **31**, 765 (1925).

[16] Fowler, A., *J. Chem. Soc.*, **1928**, 777.

Experimental data confirming the existence of definite atomic energy states are now abundant. The stepwise excitation of atoms by the impacts of electrons carrying definite amounts of kinetic energy was mentioned in Chapter 1. This stepwise production of various spectral lines in succession has, since the pioneering experiments of Franck and Hertz, been carried out in the case of many elements. For example, Schulze[20] has excited argon in seven stages. The method offers great experimental difficulties and the literature contains many discrepancies in the values assigned to the various resonance potentials of the elements by modifications of this method.

The various spectral lines or groups of lines may be also produced in an analogous step-wise manner by carefully controlled thermal excitation of the elements. In the Pasadena laboratory of the Mt. Wilson observatory, King volatilized the metals in a graphite tube electrically heated in a specially designed furnace to temperatures not far below that of an electric arc. He showed[21] that calcium vapor yields a line at 4227A at relatively low temperatures, and that lines at 3969 and 3934A appear only at temperatures above 2400°C. He has also given[22] temperature classifications of the lines of strontium, barium, magnesium, iron, titanium, vanadium, chromium, cobalt, nickel, manganese, scandium and many other elements. In the case of iron, he has grouped 902 lines according to their occurrence or absence when the temperature is 1600-1700°C., 2000°C., or 2500-2600°C. Only eleven lines are emitted at 1400°C. The method, which has also been employed by others,[23] is chiefly of value to the spectroscopist as an aid in classifying the lines into various series.

PRODUCTION OF IONS IN ULTRAVIOLET SOURCES

The chemist is familiar with ions produced as the result of electrolytic dissociation in aqueous solutions. The physicist, however, frequently encounters ions in the gaseous state, since by the application of high temperatures, electric discharges or certain radiations, it is possible so strongly to excite an atom that one or more of its electrons is sent to an orbit extremely far from the nucleus. Since the attractive force of the nucleus becomes insufficient to hold the electron in a far distant orbit, it becomes lost to the atom, and shoots out into space where, as a minute particle, it behaves as an independent unit, and is one of the particles making up an "electron gas." The atom which has lost the electron or electrons is called an ion.

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[17] Heisenberg, W., *Z. Physik*, **33**, 879 (1925).

[18] Schrödinger, E., *Ann. Physik*, **79**, 361, 489, 734 (1926); *Phys. Rev.*, **28**, 1049 (1926).

[19] De Broglie, L., Phil. Mag., **47**, 446 (1924); *Ann. de Phys.*, **3**, 22 (1925).

[20] Schulze, R., *Z. Physik*, **56**, 378 (1929).

[21] King, A. S., *Astrophys J.*, **28**, 389 (1908); **29**, 381 (1909)

[22] *Ibid.*, **29**, 190 (1909); **48**, 13 (1918); **51**, 179 (1920)· **37**, 239 (1913); **56**, 318 (1922); **39**, 139 (1914); **59**, 155 (1924); **41**, 86 (1915); **60**, 282 (1924); **42**, 344 (1915); **53**, 133 (1921); **54**, 28 (1921); **65**, 86 (1927); **89**, 377 (1939).

[23] Paton, R. F., and Rassweiler, G. M., *Phys. Rev.*, **33**, 16 (1929); Ritschl, R., *Ann. Phys.*, **13**, 337 (1932); Schüler, H., *Z. Physik*, **37**, 728 (1926).

The work necessary to remove an electron from an atom is greater than that required to displace it to any of the hypothetical orbits representing the stationary energy states of the atom. It is the ionizing work; when expressed in electron-volts, commonly shortened to volts, it is called the ionization potential. It is greater than any of the potentials corresponding to the excited states. In the case of mercury, it is 10.4 volts.

To ionize an already excited atom requires less work than is needed in the case of an atom in its stable state. To ionize a hydrogen atom which is already excited to a high energy level requires less energy than to ionize one excited only to a lower energy level. The difference between the amounts of energy required for ionization in these two cases represents the amount of energy required to raise the atom from the lower to the higher stage of excitation. This would be the amount of energy emitted in a spontaneous return of the atom from the higher to the lower energy level. By multiplying the frequency of the emitted line by the Planck constant, the value of this energy is obtained in ergs.

By both the spectroscopic method and the method of studying the effects on atoms of impacts of electrons accelerated by electric potential gradients, physicists have obtained a large amount of information regarding the energies required to excite atoms of most of the elements to various energy levels, or to ionize them. The detailed results have been summarized by Bacher and Goudsmit.[24] The ionization potentials of a few of the elements most frequently employed in sources of ultraviolet rays are given in Table 1, which also includes for some a resonance potential and the energy required to expel a second electron from an ion of the atom.

Table 1.--Resonance and Ionization Potentials of Various Elements.

Element	Resonance Potential (volts)	*Ionization* Atom.	*Potentials of* Ion
		(volts)	(volts)
Hydrogen	10.4	13.5	....
Helium	20.4	24.46	....
Carbon	....	11.2	24.3
Nitrogen	8.2	14.5	29.5
Neon	11.8	21.5	40.9
Sodium	2.1	5.1	....
Argon	13.2	15.7	27.8
Mercury	4.9 (6.67)	10.38	18.65

Energy-Level Diagrams. The transitions permissible between the energy states of an atom are most readily set forth in diagrams called energy-level diagrams or Grotrian diagrams.[25] These serve also to indicate the energies in the various levels. Such a diagram for mercury is given in Figure 4.

A horizontal line at the top of the diagram represents the energy of the ion, which is arbitrarily taken as zero. A dot placed near the bottom of a vertical line at the left of the diagram indicates the energy of the stable or normal state of the atom. The distance at which it is located below the zero energy state of the ion on a suitable scale represents the energy which must be put into the atom to ionize it. Since the atom in its normal state has less energy than the ion, which is arbitrarily taken as zero, the energy associated with the atom or with any state of excitation less than ionization, is considered to have a negative value. The energy values are frequently expressed in electron-volts, since in many cases the

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[24] Bacher, R. F., and Goudsmit, S., "Atomic Energy States," New York, McGraw Hill Book Co., 1932.

[25] Grotrian, W., "Graphische Darstellung der Spektren von Atomen und Ionen mit ein, zwei, und drei Valenzelektronen," 2 vols., Julius Springer, Berlin, 1928.

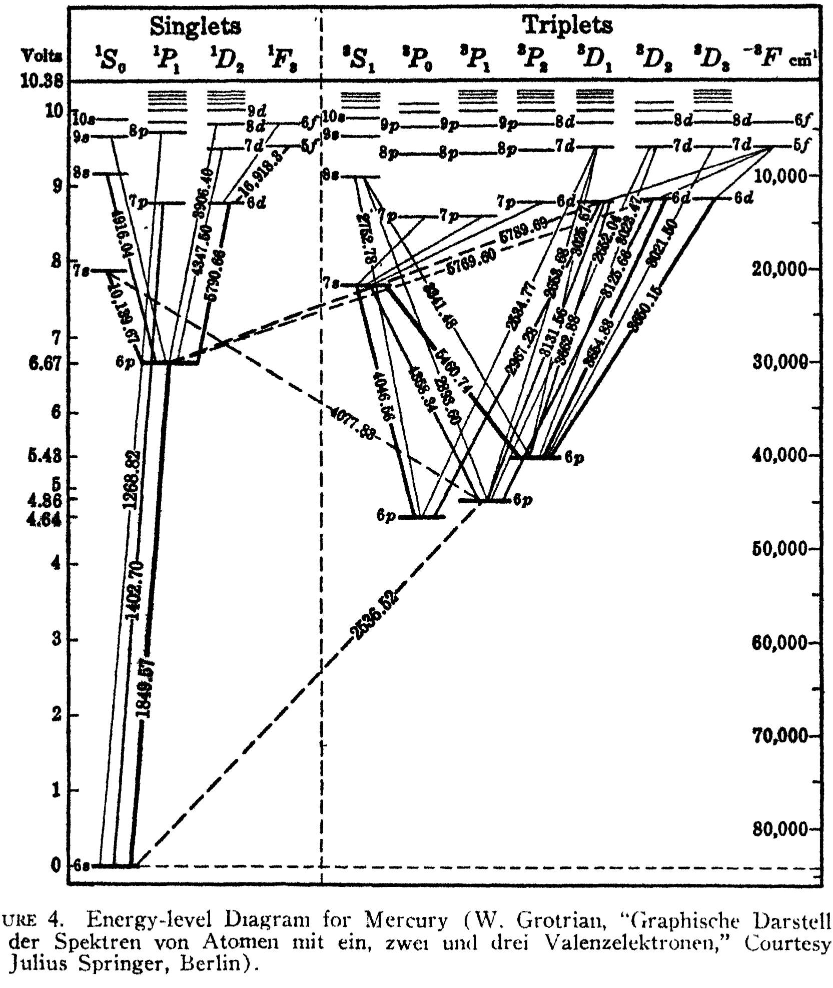

FIGURE 4. Energy-level Diagram for Mercury (W. Grotrian, "Graphische Darstellung der Spektren von Atomen mit ein, zwei und drei Valenzelektronen," Courtesy of Julius Springer, Berlin).

information was obtained by the method of critical potentials. As the diagram is also intended to yield the frequencies of lines emitted during transitions from one state to another, it is convenient to employ also a vertical scale giving the frequencies corresponding to the various energy states. This can be obtained by dividing the energies in ergs by Planck's constant *h*. Division by the velocity of light converts these frequencies into the more convenient wave-numbers. Usually, the levels are determined spectroscopically by multiplying the wave-number of the line by *hc* to obtain the increment of energy between the energy levels.

Energy-levels for each of the S, P, D and F terms are designated by short horizontal marks. Doublets, triplets, etc. are indicated by using separate columns for each member of the multiplet. The state of excitation for each electron is usually denoted by giving the principal quantum number as a numeral for each short horizontal line marking an energy state.

Diagonal lines are drawn connecting the various states in accordance with the selection principles. The difference between the wave-numbers of the states connected by a diagonal line yields the wave number of the spectral line. Transsitions between terms of unequal multiplicity are called intercombination lines. They violate the selection rule that when J is 0, its value must change. It happens, however, that the prominent mercury resonance line, 2537A, is such an intercombination line.

Chapter 3

Survey of Sources

The various sources of ultraviolet radiations are all devices for the application of energy to atoms and molecules, usually in the vapor or gaseous states, for the purpose of exciting them to higher energy-levels. The differences between the many types of apparatus lie in the choice of the atoms which are excited, in the form of energy applied for the excitation, and in the means adopted for its application.

Once the excitation has been effected, the excited atoms or molecules retain their increments of energy for a brief period and then revert to states of lower energy, emitting their extra energy as radiation. The duration of the excited states may be altered somewhat by varying the pressure of the gas or by adding an inert gas.

The natural source of radiations, the sun, is discussed in Chapter 11, following a consideration of filters, since atmospheric filtration prevents some of its radiations from reaching the surface of the earth. The most important artificial sources of ultraviolet rays are the arc, spark and glow discharge. In the following paragraphs the chief points of distinction between these types of discharge will be described, after which other less widely used sources will be considered.

The passage of a direct current discharge through gases at low pressures frequently gives rise to the glow discharge, the well-known phenomenon observed in a Geissler tube. In it, various parts of the tube assume characteristic appearances known as the cathode glow, the Crookes dark space, the negative glow, the Faraday dark space, the positive column and, when present, the anode glow.

The arc is a discharge of electricity through a gas, which may be at any pressure, under conditions such that one or both of the electrodes becomes heated and by vaporization contributes a stream of gaseous material which aids in the conduction of the current (direct or alternating) across the space. In these two forms of discharge—the glow and the arc—the impressed voltage is usually low, as compared with the very high voltages employed for the spark discharge. In the arc, the potential drop in the region of the cathode is usually very low, of the order of tens of volts, but in the glow, it is of the order of hundreds of volts. In practice, the spark usually involves the very brief oscillatory discharge of some form of condenser across an air-gap, with the production of light and heat. With suitable equipment, a series of very rapidly repeated discharges may occur with the production of a loud sound.

Close to the cathode in a glow discharge in nitrogen at 0.5 mm. pressure[1] is a narrow dark space (Crookes dark space), followed by an intense negative glow region which decreases in intensity to the Faraday dark space, several times wider than the cathode dark space. This is followed by the bright positive column which begins sharply at a definite position and extends, usually with uniform intensity, toward the anode. Under certain conditions, the positive column may be striated. There may also be an anode glow. The positions between the boundaries of these various regions are determined by the cathode, since they are changed if the cathode is moved within the discharge tube but are not affected by moving the anode. If the anode is made to approach the cathode, the length of the positive column decreases. It is possible to eliminate the latter completely and have the anode located within the negative glow or in the cathode dark space.

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[1] This discussion of the glow discharge is based upon one by Dushman, S., *Elect Eng.*, **53**, 1204, 1283 (1934); see also Found, C. G., *Trans. Illum. Eng. Soc.*, **33**, 161 (1938).

The potentials with respect to the cathode at various points may be determined by the use of exploring wires or electrodes introduced into the various regions, a method employed by Stark, Retschinsky and Shaposchnikoff [2] and placed upon a sound theoretical foundation by Langmuir and Mott-Smith.[3] The use of this "probe" method has been of great value in advancing our knowledge of the mechanisms occurring in gaseous discharges, as it is capable of yielding information as to the potential distribution, the densities of ions and the mean kinetic energies of the free electrons.

Close to the cathode is a narrow region in which there is a steep potential gradient, the drop varying from 60 to 400 volts, depending on the nature of the gas and the cathode. Much of the entire discharge voltage drop occurs in this region. In the Faraday dark space there may be a slight positive or even a negative gradient. Throughout the positive column, the gradient is constant, so that the total voltage drop in the tube depends upon the length of the positive column as well as upon the cathode fall. In the glow discharge, there is little change in voltage at the anode. Compton and Morse [4] assume the large amount of energy consumed in the cathode fall to be used in accelerating positive ions toward the cathode. By bombarding the cathode, these liberate electrons; the liberated electrons while close to the cathode receive enough energy to enable them on striking atoms to produce more positive ions, and so continue the process. These authors calculate that an electron makes about ten such ionizing collisions in passing through the region of the cathode fall, and consider that most of the current at the surface of the cathode is carried by positive ions.

The large drop of 300 or more volts in this region may be lessened by employing some accessory method of inducing the cathode to emit electrons, such as heating it to produce thermionic emission or irradiating it with ultraviolet light to cause photoelectric emission. By such methods the cathode drop may be reduced to a value related to that of the ionization potential or of a resonance potential of the gas.

The remaining space between the electrodes is called the plasma, a term also used in the case of arcs. Langmuir [5] showed that the thickness of the cathode sheath is of the order of 0.01 mm. Electrons from the cathode are accelerated in this sheath and carry their energy into the plasma where most of the emission of light occurs. Electrons which have acquired the energy of the cathode drop V_c (electron-volts) are called primary electrons. Such a primary electron on striking a gas atom may lose to it by inelastic impact the energy required for ionization, V_I. It then has left the energy $V_c - V_I$ and is called a secondary electron. Its energy may still be sufficient to excite certain atoms, depending upon their resonance potentials. When the electron after such collisions no longer has enough energy to excite atoms by impact, it is called an ultimate electron.

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[2] Stark, J., Retschinsky, T., and Shaposchnikoff, A., *Ann. Physik*, **18**, 213 (1905)

[3] Langmuir, I, and Mott Smith, H. Jr, *Gen Electric Rev*, **27**, 449, 538, 616, 762, 810 (1924) For recent developments of the theory of the probe method, see Davydov, B I., and Zmanovskaya, L I., *J. Tech Phys (U.S S R)*, **6**, 1244 (1936); Emeleus, H. J and Brown, W L., *Phil. Mag*, **22**, 898 (1936); Polin, V, and Gvozdover, S, *Physik Z. Sowjetunion*, **13**, 47 (1938); *Chem. Abs.*, **32**, 4422 (1938); Yankin, G M., *J Tech Phys. (U S.S.R.)*, **8**, 45 (1938), *Chem. Abs.*, **32**, 5692 (1938).

[4] Compton, K. T, and Morse, P. M., *Phys. Rev*, **30**, 305 (1927). For recent observations on the cathode region, see Brewer, A. K., and Westhaver, J. W, *J Applied Phys.*, **8**, 779 (1937); Güntherschulze, A., and Betz, H., *Z Physik*, **108**, 780 (1938).

[5] Langmuir, I, *Phys. Rev.*, **33**, 954 (1929).

Although in this discussion, it has been assumed that the cathode is cold and need not contribute any metallic vapor to the glow, it is possible under certain conditions to have a glow discharge from a molten cathode. Although the glow form of discharge is most commonly produced in gases at low pressures, nevertheless it may be produced under some conditions at atmospheric pressure if the current carried by the discharge is kept at only a few milliamperes. As the current is increased beyond a certain limiting value, usually about 0.1 ampere, the glow suddenly changes to an arc. In the arc discharge, the cathode current density is from a hundred to a thousand times that in the glow discharge, and the restricted spot from which the current issues may be very hot. It was for a time generally believed that high temperatures near, if not at, the cathode were essential for the maintenance of an arc.[6]

It has, however, been shown that the mercury-vapor arc can be operated with the cathode maintained at −70°C. or lower, the voltage being not much higher than in normal operation of the arc.[7] Apparently exceptions to general rules are so frequent and the number of borderline cases so great that rigid definitions of the forms of gaseous discharge are scarcely attainable. The following were suggested by Thomson:[8]

Glow. A discharge between cold electrodes, the current being carried entirely by gaseous ions and electrons.

Arc. A discharge in which the current is carried by the material of the electrodes as well as by the gas between them.

Spark. The initial unstable stage in any discharge between cold electrodes

Spark and Arc Spectral Lines. The spectra produced by an arc and by a spark between similar electrodes may differ widely in character. An understanding of the origin of this difference, which is fundamental both historically and theoretically in the origin of atomic spectra, is essential to the employment of these sources in spectrographic methods for detection of the elements. Lockyer, a pioneer in solar spectroscopy, discovered that the intensities of certain lines occurring in the arc spectra of many elements are enhanced in their spark spectra.[9] In some cases, lines occurring in the arc spectrum are missing in the spark spectrum; on the other hand, the spark spectrum may show lines not present in the arc spectrum. Lockyer demonstrated the appearance of new or "enhanced" lines in the spectra of stars, particularly in the Novae, and believed that they indicated the existence of hitherto unknown elements capable of existing only at the enormous temperatures of the stars, or under the conditions of temperature found in the spark. It has since been shown that "spark" lines can also be produced by the high temperature excitation of certain elements in a resistance furnace.

The key to the nature of these assumed new elements was given in Bohr's earliest paper on the theory of atomic structure. In 1897, Pickering had discovered in the spectrum of a certain star, besides the Balmer lines of hydrogen, a series of new lines, each of which lay about midway between two lines of the Balmer series. Their frequencies could be represented by the Balmer formula if for 3, 4, etc. in the second term, there were substituted 3.5, 4.5, etc. As he believed the new lines to be due to hydrogen, Pickering altered the Balmer formula to include them by making the Rydberg constant four times its usual value. The new lines were not, however, encountered in spectra excited in the laboratory until Fowler in 1912 observed them in the spectrum of a discharge tube containing both hydrogen and helium. Bohr realized that if a helium atom should lose an electron the resulting ion would resemble the hydrogen atom, except for the fact that its nucleus would bear two positive charges rather than one He appreciated the necessity of incorporating the number of nuclear charges, *i.e.*, the atomic number, in his equation for the calculation of the energy associated with the rotation of an electron in an orbit, the expression which in his theory yields the Rydberg constant. As this expression involves the square of the nuclear charge, the result yields a constant four times as great when there are two nuclear charges as when there is but one. The constant for the helium spectrum would, therefore, be four times that for the hydrogen atom. This led Bohr to suggest that the Pickering lines are emitted by helium ions rather than by hydrogen, an explanation which met with much opposition until it was found that the lines could be observed in pure helium when suitably excited.

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[6] For discussion, see Slepian, J., *J. Frank Inst*, **1926,** 79; *Phys. Rev*, **27,** 407 (1926)

[7] Kawa, J, *Acta Phys. Polonica*, **1,** 427 (1932); Newman, F H, *Phil Mag.*, **18,** 607 (1934)

[8] Thomson, J., *Phil. Mag.*, **13,** 824 (1932); see also Mckeown, S S., *Phys Rev*, **34,** 611 (1929) and Kaiser, H., and Wallraff, *Z Physik*, **112,** 215 (1939) for transitions between the forms of discharge.

[9] Lockyer, Sir Norman, *Proc. Roy Soc*, **30,** 22 (1879)

It is more difficult to excite helium to emit the Pickering lines than it is to cause this element to emit the ordinary lines observed in the glow discharge. In order to form the ion and induce it to emit energy, spark excitation is used. In general, spectra of the ions of elements are commonly called spark spectra, as distinguished from the arc spectra from the atoms of the same elements. These designations must not be taken too literally, since the so-called "spark" spectra of many elements may be produced by other means of excitation. Some lines of a spark series frequently appear in arc spectra, although they may be enhanced in intensity in the spark spectra of the same elements.

It has been noted that the spark spectrum of helium resembles the arc spectrum of hydrogen, the preceding element of the periodic table, the only difference being that the Rydberg formula must be altered to take account of the extra nuclear charge. Similar relations hold throughout the periodic system. The alkaline earth elements have two electrons in the outer ring. Loss of one of these on ionization causes the atom to resemble that of the preceding alkali metal and to give a spectrum like it when the excess nuclear charge is taken into account. The multiplicities of the ions of elements are closely related to those of the atoms of the preceding elements of the periodic table.

It is also possible to observe under suitable conditions spectra from doubly charged ions, or atoms which have lost two electrons. In some instances, still higher degrees of ionization have been studied. To distinguish between these spectra, Roman numerals are employed after the symbol of the element. Thus, C I refers to the spectrum of the neutral carbon atom, C II to that of the ion C^+, C III to that of the doubly charged ion C^{++} and C IV to that of triply ionized carbon, C^{+++}. These are spectra of various orders, C I being of the first order. A given element excited by various methods produces different spectra, in each of which lines corresponding to one or another of these stages of ionization predominate. The demarcations are not sharp and it is common to find faint lines representing a higher degree of ionization superposed upon a spectrum of lines representing a lower stage of ionization. Antimony excited by a vacuum spark yields predominantly lines due to the doubly ionized atom Sb III. Tin in a Paschen hollow cathode in a discharge tube emits the lines of Sn II.[10]

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[10] Lang, R. J., *Phys Rev*, 35, 445 (1930).

In the atmosphere of the sun most of the elements are in the atomic state and yield the arc spectra. Spark lines are, however, observed in the case of a few easily ionized elements such as calcium. In the spectra of some stars, lines are found indicative of the presence of singly, doubly or further ionized ions. The appearance of lines of this character serves as a scale by which such bodies may be classified according to their temperatures. In the interiors of some of the stars, the temperatures reach millions of degrees and completely stripped atoms—mere nuclei—are believed to exist.

OTHER SOURCES OF ULTRAVIOLET RAYS OF LESSER IMPORTANCE

Incandescent Solids. The Nernst glower is said to yield a faint spectrum even beyond 2500A. Not for many years, however, has it been employed as a source of ultraviolet rays.[11]

Since about 1920, the incandescent tungsten lamp, operated at an abnormally high filament temperature, has been employed occasionally as a source of continuous ultraviolet rays for absorption studies. Lamps intended for this purpose, and provided with special quartz bulbs or windows, were described by Gehlhoff,[12] Franck and Grotrian,[13] and by Stockbarger.[14] Also, Stockbarger, Dingee and Burns [15] have presented spectrograms showing that automobile headlight bulbs operated at a filament temperature of 3400°K. (at which they last but a few hours), permit the detection of radiations less than 3000A when the bulbs are of lead glass. With soda-lime glass bulbs, emission to 2900A could be detected, and measurements indicated that 0.046 per cent of the energy emitted through such bulbs lies below 3170A. As this was over three times the amount of radiation expected in this region from the laws of black-body radiation, they concluded that there is a selective ultraviolet emission.

Luckiesh [16] presented calculations of the percentages of the total emission which lie between 2800 and 3200A from tungsten filament lamps of various wattages at several temperatures. His results indicated that such lamps would not be very effective sources for supplying this band of radiations to children. For the same total energies a quartz mercury arc gives 175 times as great an output in this region as does a tungsten filament lamp. Later calculations by Forsythe and Christison [17] were more favorable. By utilizing data of Hulburt [18] on the percentages of the total emissivity at 3400, 3800 and at 4200A at various temperatures up to 2800°K. and employing certain considerations relating to the color temperature of tungsten, Forsythe and Christison obtained a curve for the spectral emissivity of tungsten at 2800°K. from the infrared to 2700A. By a step-by-step integration, they secured from this curve values for the relative amounts of energy in various portions of the spectrum. From these values (at several temperatures) and the total wattages of the lamps were calculated theoretical amounts of energy in these spectral regions falling upon a square centimeter of surface at a distance of one meter from the filament. The absence of any absorbing bulb surrounding the filament was assumed. It was found that a 500-watt tungsten lamp burning under conditions giving a life of 1000 hours would yield a total energy of 4 milliwatts per square centimeter, of which 0.0013 milliwatt was of wave-lengths shorter than 3250A and 0.00044 milliwatt was between 3100 and 2900 A. When the lamp was burned under 100-hour life conditions, the values were, respectively, 4.00, 0.0017 and 0.00060. A 900-watt motion-picture lamp gave 9.2, 0.0076 and 0.0028 milliwatts. These values compared favorably with the energy of the sunlight passing through an air-mass of 2.37 atmospheres, which gave 0.010 milliwatt of energy shorter than 3250A and only 0.00017 between 3100 and 2900A. The total energy of the sunlight was, however, far greater, 33.9 milliwatts.[19]

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[11] Coblentz, W. W., *Bur. Standards Bull.*, **9**, 103 (1913); Griffiths, H. D., *Phil. Mag.*, **50**, 263 (1925).

[12] Gehlhoff, G., *Z. tech. Physik*, **1**, 224 (1920).

[13] Franck, J., and Grotrian, W., *Z. tech. Physik*, **3**, 195 (1922).

[14] Stockbarger, D. C., *J. Opt. Soc. Am.*, **9**, 337 (1924).

[15] Stockbarger, D. C., Dingee, A. L., and Burns, L., *J. Opt. Soc. Am.*, **18**, 53 (1929).

[16] Luckiesh, M., *J. Frank. Inst.*, **206**, 60 (1928).

[17] Forsythe, W. E., and Christison, F., *General Electric Rev.*, **32**, 662 (1929).

[18] Hulburt, E. O., *Astrophys. J.*, **45**, 149 (1917).

Borstler [20] proposed the therapeutic use, by means of a quartz applicator, of ultraviolet radiations from a 6- or 8-volt tungsten automobile headlight in a Pyrex bulb, operated at voltages 10 per cent above normal.

Flames. As sources of ultraviolet radiations, flames are of little value. They are employed occasionally in conjunction with sparks in certain methods of quantitative analysis by spectrographic methods. In the early work in the visible region, flames were used as a ready means of vaporizing salts and exciting the metallic portions thereof, particularly the alkalies, which readily give characteristic lines.[21] To make the method available for the detection of elements more difficult to excite, higher temperatures are necessary. Early students of line spectra [22] secured these by directing an oxyhydrogen blowpipe upon the solid to be examined. Still higher temperatures may be attained with the aid of the oxyacetylene flame.[23] The spectrum produced in the flame itself is sometimes a complicating factor. It is a band spectrum emitted by the molecules of water vapor produced during combustion. The lines of these bands are weak at wave-lengths greater than 3200A and interfere but little with analyses based upon lines situated at longer wave-lengths.

Before the development of the mercury arc or the appreciation of the value of other simpler arcs, flames were occasionally employed as sources in the study of reactions produced by ultraviolet rays. Wulf employed a flame of carbon disulfide and oxygen for such purposes.[24]

Bombardment by α-rays [25] or cathode-rays [26] has been used in investigations in the region of wave-lengths longer than those of the usual x-rays.

Among the less important electrical sources of ultraviolet radiation is the exploded wire method of Anderson [27] although it has occasionally been of service in the study of the absorption spectra of vapors. In this method, a fine wire (less than 36-gauge), 5 cm. in length, of nickel, iron, manganese or copper, is fused or exploded by discharging through it a heavy current by means of a large condenser charged by a 500-watt, 26,000-volt transformer, suitably rectified. In series with the wire is an adjustable spark-gap. In air, the method yields a nearly continuous spectrum, with many dark lines, due to absorption by the hot metal vapor.

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[19] For other data on the emission of tungsten filaments, see von Alphen, H. C., *Ann. Physik*, **85**, 1058 (1928) and Hoffmann, F., and Willenberg, H., *Physik. Z.*, **35**, 713 (1934)

[20] Borstler, E. W., U. S. P. 1,800,277, April 14, 1931.

[21] For a general discussion, see Lohse, H. W., *Can. J. Research*, **12**, 519 (1935), and Lundegård, H , *Lantbruks-Högskol Ann* , **3**, 49 (1936).

[22] Lockyer, Sir N., and Austen, R., *Proc Roy. Soc.*, **23**, 344 (1875); Liveing, G. D., and Dewar, J., *ibid.*, **28**, 352 (1879), Hartley, W. N., *Phil. Trans.*, **185A**, 161, 1047 (1894).

[23] Hemsalech, G. A., and de Watteville, C., *Compt. rend.*, **149**, 1112, 1369 (1909); de Gramont, A., *ibid.*, **157**, 477 (1918); **176**, 1104 (1923).

[24] Wulf, T., *Ann. Physik*, **9**, 946 (1902).

[25] Greinacher, H., *Z. Physik*, **47**, 344 (1928).

[26] Cohn, W. M., *Z. Physik*, **70**, 662, 667, 679 (1931).

[27] Anderson, J. A., *Astrophys. J* , **51**, **37** (1920).

In place of wires, asbestos fibers may be used upon which solutions of the various alkaline-earth chlorides to be analyzed have been evaporated.[28]

A very brilliant light (up to 14,000,000 candles) of extremely short duration (less than 5 millionths of a second) is said to be produced by the explosion in argon of 0.4 cc. of a liquid explosive, such as tetranitromethane. Its spectrum extends far into the ultraviolet.[29]

Electrodeless Discharge. The high-frequency electrodeless discharge has been but rarely employed for carrying out photochemical reactions. Since its discovery by Hittorf in 1884, there has been much discussion as to whether the phenomenon is to be ascribed to an electrostatic or an electromagnetic field.[30]

Apparently either can excite a gas or vapor at low pressure to emit a brilliant diffuse discharge. In these methods, the oscillatory discharge from a condenser goes through a coil of wire surrounding but not touching the reaction vessel. At higher gas pressures, the discharge alters in character and assumes a ring form, the lines changing from a mixture of arc and spark lines to a spectrum in which spark lines predominate. Harkins[31] used a coil of six turns of copper wire around a quartz or "Pyrex" flask with a side-tube arranged for the collection of the products formed during the passage of the discharge through various organic gases. A window was arranged for spectrographic observations of the products transiently produced. The frequency of the circuit was 800 kilocycles per second. The circuit included a 1 k.v.a. Thordardsen transformer which supplied a maximum of 25 kilovolts, a spark gap of cylindrical zinc electrodes adjustable by a screw, and a 0.025 microfarad condenser. In the discharge, both benzene and acetylene were found to be dissociated, giving spectrographic evidence of the presence of H, C, C^+, C_2 and CH. Polymerization led to compounds of very high molecular weights which appeared as solid, reddish brown flakes. At a pressure of 0.02 mm., 5000 liters of benzene vapor were passed into the flask without changing the character of the discharge; from one to two grams of solid products were formed per hour.

Another type of apparatus[32] is that in which rare gases, especially krypton and xenon, in a vessel at low pressure are subjected to an electric current or electromagnetic field of high intensity by a high frequency coil. It has a quartz window for ultraviolet irradiation processes so disposed as to be practically outside the high-frequency field. The rare gases emit a gamut of rays from the visible to the very short ultraviolet of value in therapy. The surrounding solenoid is placed far enough from the window so that the latter does not become very hot, permitting the application of the source very close to the part of the body to be irradiated. This lessens the loss of short ultraviolet rays by absorption by the air. The ends of the solenoid wire are joined to a high-frequency apparatus, such as a spark-gap diathermy apparatus. In the discharge in neon, the current density is important, as neon at high current densities emits intensely between 3350 and 3700A.[33] At current densities greater than three amperes per square centimeter, the source emits a spark spectrum, high frequency not being required.

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[28] Sawyer, R. A., and Becker, A. L., *Astrophys. J.*, **57**, 98 (1923).

[29] Michel-Lévy, A., and Maurarour, H., *Compt. rend.*, **200**, 543 (1935).

[30] Stuhlman, O., Jr., and Whitaker, M. D., *Rev. Sci. Instruments*, **1**, 772 (1930); Rayleigh, Lord, *Proc. Roy. Soc.*, **150A**, 34 (1935). For the construction of light sources of this sort in the laboratory, see Winans, J. G., *Rev. Sci. Instruments*, **9**, 203 (1938).

[31] Harkins, W. D., *Trans. Faraday Soc.*, **30**, 221 (1934).

[32] French P. 743,167, March 25, 1933, to Soc. anon. pour les Applications des Gaz Rares à la lumière, procedés George Claude; British P. 385,835, Jan. 5, 1933; *Brit. Chem. Abs.* **B**, *1933*, 197, *Chem. Abs.*, **27**, 3671 (1933). Goude-Axelos, J., and Claude, A., *Compt. rend.*, **194**, 132 (1932).

[33] Soc. anon. pour les Applications des Gaz Rares etablissements Claude-Paz and Silva, British P. 404,271, Jan. 8, 1934.

The sparking potential in electrodeless discharge tubes diminishes when the tube is illuminated by ultraviolet or visible light[34]

Radiations produced in metal vapors by the passage of radiations from another source or those furnished by active nitrogen or hydrogen, although theoretically important, do not at present constitute practical sources of ultraviolet radiations.

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[34] Zouckermann, R., *Compt rend*, **206**, 331 (1938).

Chapter 4

The Spark as a Source of Ultraviolet

The electric spark is rather infrequently used as a source of ultraviolet radiations for effecting photochemical reactions, although it has been employed in some of the more important investigations. The electric spark finds its chief application as a source of a many-lined spectrum suitable for studying absorption spectra of compounds possessing broad absorption bands. (See also Chapter 9.) It is also widely employed as a means of exciting to emission materials to be analyzed by spectrographic methods. Sparks passed in vacuum have yielded information of importance in the region of the extreme ultraviolet. The high tension disruptive electric spark between iron terminals is very rich in ultraviolet radiation and is useful in producing fluorescent effects, particularly in mineral and drug analyses. It is, however, seldom used for this purpose.

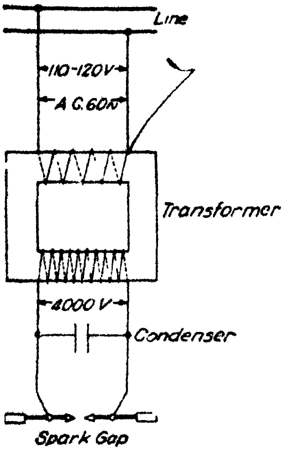

FIGURE 5.

Diagram of Connection, Iron Spark Apparatus

(Courtesy General Electric Co)

Iron electrodes were used in a spark outfit designed by Andrews.[1] The connections of the apparatus are shown in Figure 5. A small transformer steps up a 60-cycle, 110-120 volt, alternating current to about 4000 volts. A condenser is connected in series with the iron terminals. The spark gap is adjustable Assembled apparatus is shown in Figures 6 and 7. As this apparatus uses only about 250 to 300 watts, it can be safely connected to any alternating current lighting circuit.

Ross[2] recommended the use of aluminum terminals, which yielded an intensity of ultraviolet radiation (measured by the liberation of iodine from potassium iodide) twice as great as that resulting when terminals of any other common metals were used. Cadmium was not recommended because of its softness. The terminals were 3 mm. × 8 mm. in cross-section and were placed 7 cm. apart on iron plates. Small dishes, containing ice and resting on the metal, served to conduct away the heat rapidly.

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[1] Andrews, W. S., *General Electric Rev.*, April, 1916, 319.

[2] Ross, W. H., *J. Am. Chem. Soc.*, **18**, 786 (1906).

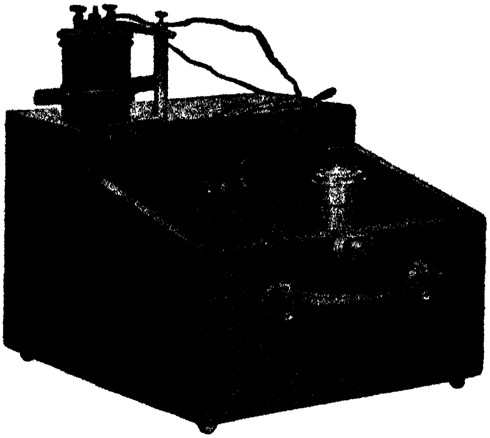

FIGURE 6.

Rear View of "Iron Spark" Apparatus.

(Courtesy General Electric Co.)

ELECTRICAL CIRCUITS EMPLOYED FOR THE PRODUCTION OF SPARKS

When a small potential difference is impressed upon two parallel electrodes separated by an air space, a very small current will be carried across the gap by the few ions present in the air as a result of cosmic rays, radioactivity, etc. As the potential difference is increased, the current increases in accordance with Ohm's law but only so long as the potential difference remains small. With further increases, the current increases less and less rapidly and finally becomes constant (saturation value) over a wide range of impressed potential differences.

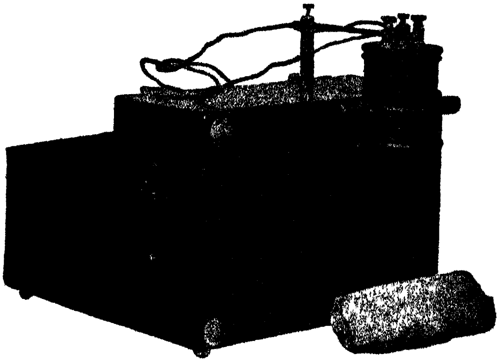

FIGURE 7.

Front View, Portable "Iron Spark" Apparatus.

(Courtesy General Electric Co.)

This occurs because the electrons in a dense gas collide with gas molecules before the electrons can acquire sufficient kinetic energy (from the potential field) to ionize the gas. Thus no new carriers of current are produced.

When the potential difference has been raised to several thousands of volts, ionization by electron impact occurs suddenly and the current rapidly attains high values. There is a brilliant flash, a spark passes across the gap with the production of a high temperature and the potential difference is temporarily obliterated.

The spark is very brief in duration. What happens following it depends on the nature of the external circuit. Under suitable conditions, the air becomes ionized, the resistance drops, and some form of self-maintained discharge ensues. This may take the form of an arc if the heat of the spark has brought the electrodes to a sufficient temperature. To produce sparks across small gaps, gradients of about 30,000 volts per centimeter are required.[3] The earliest workers to study spark spectra [4] used an induction coil to produce the necessary high potentials. By photographic methods, with rapidly moving films, Schuster and Hemsalech [5] showed that the emission of metal lines was due to an oscillating discharge, and that, following a single discharge through the air, which vaporizes the electrode material, the lines form near the electrodes and then cross the gap at rates of 400 to 1300 meters per second. The particles composing the streamers were found to be electrically charged.[6]

Studies with rotating mirrors have shown that a break in the primary circuit of the induction coil causes a series of secondary discharges, the first of these secondary discharges being bright and the others faint. The first is a true spark, since it may be shown (by the oscillograph) to follow upon a very high potential difference between the terminals of the secondary winding Such a discharge, repeated at each interruption of the primary current, emits a spectrum which is characteristic of the gas through which it passes, and exhibits but a few faint lines from the metal of the electrodes. Early spectroscopists spoke of this spark as "uncondensed," a term now known to be incorrect, since all sparks are associated with a condenser discharge. In this case the condenser was the air-gap itself together with the capacity of the secondary winding. In all sparks, the discharge is oscillatory because of the inertia effect of self-induction in the winding Most workers, however, employed a condenser (in parallel with the spark gap) charged by the induction coil to the necessary sparking potential. (Figure 5.)

The induction coil may be replaced by a small high tension alternating current transformer, thus eliminating difficulties arising in the operation of contact-breakers. As in the case of the induction coil, the capacity of the condenser determines the quantity of electricity which passes in each spark and the intensity of the spark. Only when the condenser capacity is sufficient is the discharge strong enough to vaporize the electrode material into the discharge, there to emit its characteristic lines. With condensers of high capacities, the intensity is sufficient to ionize the atoms of the electrode metal and produce the spark spectrum of the latter. The sizes of transformer and condenser must be so chosen that the sparking potential may be obtained or exceeded. Details of transformer and condenser requirements are found in a paper by Anderson [7] and in the publications of the makers of spectrographic equipment.

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[3] For further detailed discussions of spark theory, see Loeb, L. B, *Rev Modern Phys*, **8,** 267 (1936); Rogoski, W, *Z. Physik*, **100,** 1 (1936), Pirani, M, *Angew. Chem*, **44,** 395 (1931); Darrow, K. K., "Electrical Phenomena in Gases," Baltimore, Williams and Wilkins, 1932

[4] Hartley, W N., *Phil Trans Roy Soc*, I, 50 (1884); II, 327; Pollok, J. H, and Leonard, A. G., *Proc Roy Soc. Dublin*, **11,** No 16, 17, 18 (1907); No 23, 24 (1908), No 31 (1909)

[5] Schuster, A., and Hemsalech, J G., *Phil Trans.*, **193A,** 189 (1900).

[6] Milner, S. R. *Phil. Trans.*, **209,** 71, 1908, see also Royds, T., *Ibid.*, **208,** 333 (1908); *Phil Mag*, **19,** 285 (1910) Their velocities have been measured recently. Miyanishi, M, *Japan. J Phys.*, **5,** 67 (1928); *Chem. Abs*, **23,** 4404 (1929), Asami, Y, *Elec Eng. Japan*, **53,** 27 (1933); *Chem. Abs*, **27,** 2630 (1933), Toriyama, Y, and Shinohara, U., *Elec Eng Japan*, **53,** 100 (1933); *Chem Abs.*, **27,** 2630 (1933).

[7] Anderson, J A, *Astrophys. J.*, **59,** 76 (1924).

A high capacity condenser causes slower oscillations in the discharge, thereby increasing the amount of electricity secured in each oscillation. This prolongs the train of sparks and produces a heating effect on the electrodes. de Kowalsky[8] showed that the region of maximum radiated energy is displaced toward the longer wave-lengths as the oscillatory current is increased. Increasing the amount of energy consumed in the spark, however, causes displacement in the opposite direction, although this is to some extent dependent upon the nature of the electrodes. The intensity of the mean ultraviolet radiation emitted varies inversely with the frequency.

The oscillations may also be made slower by introducing additional self-inductance, the rate of oscillation varying inversely as the square root of both the capacity and self-inductance of the circuit. A self-inductance coil, called frequently a Hemsalech coil,[9] has the property of making the "air-lines" disappear, the spectrum being then largely from the electrodes. The self-inductance coil is introduced in series with the gap at A in Figure 8.

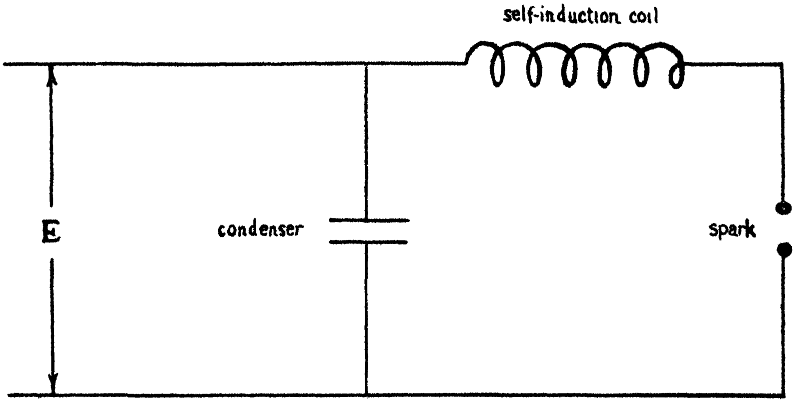

FIGURE 8 Diagram of Spark Circuit. (Twyman and Smith, "Wavelength Tables for Spectrum Analysis" London, Adam Hilger Ltd.).

The form of the discharge depends upon the amount of self-inductance employed since the latter decreases the rate of oscillations, and also lessens the current which passes in the first discharge, spreading the current more evenly over a series of oscillations. Without any self induction, the oscillations are strongly damped by the resistance of the gap, so that most of the energy passes in the first spark. With self-induction, less current passes during the first spark and the oscillations continue for a longer time.

In the first case (no self-induction), the first strong spark is believed to excite the gas and to send some vaporized metal from the electrodes. The discharge then dies away rapidly and the metal vapor cools. Subsequent oscillations are too weak to vaporize more metal. With but little metal vapor in the gap, the resistance and potential are high and the electrons acquire sufficient kinetic energy to excite the gas. With self-inductance the first spark is not strong enough to excite the gas and its lines are not evident. The cumulative effect of the subsequent discharges is, however, sufficient to heat and vaporize the metal. The introduction of this

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[8] de Kowalsky, I., *Compt. rend.*, **158**, 1337 (1914). *Bull. Soc. Int. Elect.*, **4**, 437

[9] Hemsalech, T. A., *Compt. rend.*, **122**, 285 (1899); Schenck, C. C., *Astrophys. J.*, **14**, 116 (1901); *Phil. Trans.*, **193A**, 189 (1900).

GOVERNMENT OF

heated metal vapor into the gap lowers the resistance and the potential and the electrons fail to acquire sufficient energy to excite the gas. As the metal becomes ionized when the spark carries enough current, all of the arc lines are present. The prolongation of the oscillations under these conditions led de Gramont to speak of such sparks as oscillating sparks as distinguished from the condition which he called the "condensed" spark. This is misleading for both are oscillatory and condensed in fact.[10]

The effects of variations in capacity and self-inductance are particularly important when the spark is employed as a source for the spectrographic analysis of metals. Since spectrographic analysis involves technique which requires considerable experience and since this subject does not fall within the province of this book, further details must be sought in manuals devoted to spectrographic essays. For spectrographic analysis, Scheibe and Neuhäusser recommended[11] 0.0033 mfd. capacity and 0.000015 henry of self-induction. Resonance transformers[12] and high frequency transformers have been recommended.[13]

"Hot Sparks." By employing large induction coils together with condensers of high capacity, it is possible to obtain spectra representative of high degrees of ionization. So-called "hot sparks" with very narrow gaps were employed by Millikan[14] in his work on the short wave-length spectra of stripped atoms. As the sparking was done in a vacuum, air-lines were not a disturbing feature, so that low self-inductance could be used. The intensity was controlled by an adjustable auxiliary spark-gap in series with the spark to be studied. The operation of these sparks has been described by Sawyer.[15] Robinson[16] estimates that temperatures of 300,000°K. can be attained by such methods. Edlén[17] in studying the C V spectrum at wave-lengths as short as 40.28A, employed a vacuum spark with a capacity of 0.3 μF, charged to 60,000 volts. With thirty sparks passing per minute, and a metal grating employed at a glancing angle of 5.4°, he found half an hour sufficient for an exposure.

The Arrangement of the Electrodes of Spark Sources

In studying the emission spectra of metals or alloys, it is necessary to support two blunt-pointed rods or heavy wires of the material so that a gap is formed. Adjustable supports for the rods are desirable. The spectra of minerals can be obtained by attaching them to rods by spring clips.[18]

Boas[19] passes a high speed current of air past the spark in order to destroy the aureole surrounding it. He also describes an electrostatic relay to maintain a constant distance between the electrodes. The latter erode rapidly if thin. On the other hand the spark may move from place to place on a thick electrode. Gring and Clark[20] described a stand capable of holding four pairs of electrodes, any pair of which can be quickly brought into position for exposure.

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[10] See also Negresco, T., *J. Chim. Phys.*, **25**, 308 (1928).

[11] Scheibe, G., and Neuhausser, A., *Angew. Chem.*, 1218 (1928), see also Meggers, W. F., Kiess, C. C., and Stimson, F. J., *Bureau of Standards Sci. Paper No. 444*, 1922; Sweitzer, E., *Z. anorg. allgem. Chem.*, **164**, 127 (1927); Kosbahn, T., *Ann. Physik*, **25**, 625 (1936); Gibbs, R. C., Vieweg, A., and Gaertlein, C. W., *Phys. Rev.*, **34**, 406 (1929); Langstroth, G. O., and McRae, D. R., *Canadian J. Research*, **16A**, 17, 61 (1938).

[12] Boas, H., *Z. Physik*, **60**, 690 (1930).

[13] Hull, F. A., and Steele, G. J., *Proc. Am. Soc. Testing Materials*, **27**, II (1927); Gerlach, W., and Schweitzer, E., *Z. anorg. allgem. Chem.*, **195**, 255 (1931); Potopenko, G., *Ibid.*, **215**, 44 (1933); Goroncy and Urban, Ibid., **211**, 28 (1933); Feussner, O., *Z. Metalkunde*, **25**, 73 (1933).

[14] Millikan, R. A., *Astrophys. J.*, **52**, 47 (1921); **53**, 150 (1921); *Phys. Rev.*, **12**, 168 (1918); *Science*, **19**, 138 (1919).

[15] Sawyer, R. A., *Astrophys. J.*, **52**, 286 (1920); Sawyer, R. A., and Smith, F. R., *J. Opt. Soc. Am.*, **14**, 287 (1927).

[16] Robinson, H. A., *Z. Physik*, **100**, 636 (1936).

[17] Edlén, B., *Nature*, **127**, 405 (1931).

[18] Heraeus, W. C., G.m.b.H., British P. 400,607, Oct. 18, 1933.

[19] Boas, H., *Z. Physik*, **60**, 690 (1930).

Arrangement of Electrodes. Spark sources have been employed in measuring the extent of some photochemical reactions. In such cases, uniformity over a prolonged time is necessary. Forbes and Brackett secure this by striking the spark[21] between adjacent edges of two square bars of metal (see Figure 9). The latter move in horizontal planes at right angles to each other. Conduction and radiation of heat are so rapid that erosion is at a minimum. The method avoids hand control required by previous workers with sparks and monochromators.[22] In the apparatus, flexible woven metallic bands connect two 400 × 25 × 25 mm. bars to a condenser. The bars rest in rectangular troughs perpendicular at right angles. Posts P are insulated from the base board by vulcanite blocks. The upper trough is cut away at G to expose the lower edge of the upper bar. The ends of the troughs are raised or lowered by turning the milled heads until the bars are horizontal, and their separation along the common diagonal is 2 mm. The shortest path for the spark lies along this one line. Blasts of air provided by two vacuum cleaners in tandem converge from the jets J upon the gap at G to blow back the corona. A ventilated housing conducts away oxide fumes. Threaded rods R, ending in insulating links I, pass through sleeves rotated by worm gears W, retracting the bars. The optimum speed varies with the energy of the spark and the volatility of the metal. Zinc bars, operated at 250 mm. per hour, give 1½ hours net service for each of the four pairs of edges. When a pair of edges has been used up, the current is interrupted, the oxide crusts detached, the threaded rods

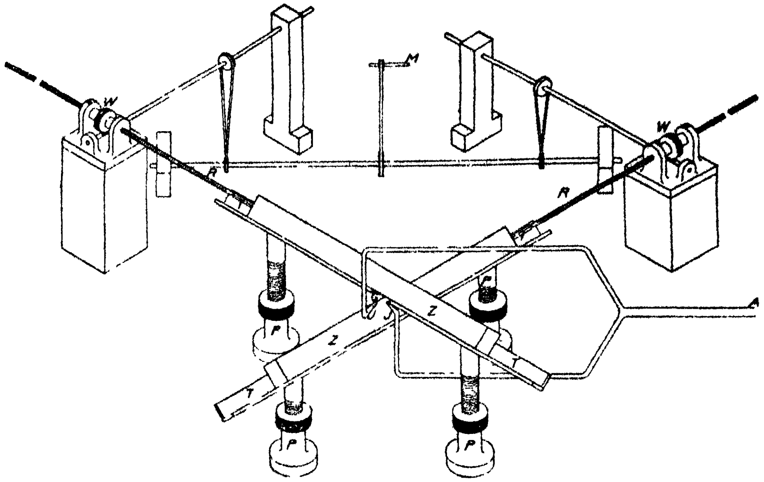

FIGURE 9. Spark Source for Automatically Constant Illumination (Forbes and Brackett, *Journal American Chemical Society*).

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[20] Gring, J. L., and Clark, G. L., *Rev. Sci. Instruments*, 7, 305 (1936).

[21] Forbes, G. S., and Brackett, F. P., Jr., *J. Am. Chem. Soc.*, 53, 3973 (1931).

[22] Warburg, E., *Sitzb. Preuss. Akad. Wiss.*, 746 (1911); Beckman, A. O., and Dickinson, R. G., *J. Am. Chem. Soc.*, 52, 124 (1930).

returned to their original positions, and operation is started with a fresh pair of edges. The depth of erosion on the upper edge is constant at 1.2 mm. for zinc and 0.5 mm. for aluminum. On the lower edge, it is about two-thirds as much. A 5 kv. oil transformer is operated at 110 volts and 35 amperes under control of a voltage regulator. The gap voltage is 6500 ± 500, secured by employing a heavy duty mica condenser of 0.04 microfarad capacity.

With the monochromator employed, it was possible to secure approximately monochromatic radiations in the case of zinc of 30,000 ergs per second at 2530A, and of 16,000 at 2080A. With cadmium, the intensities attained at the slit were 34,000 ergs per second at 2170, 79,000 at 2260, 22,000 at 2570 and 27,000 at 2710A. The intensities attainable with aluminum electrodes were lower. Forbes[23] regarded the spark as an almost indispensable source of radiations of wave-lengths shorter than 2500A. He noted that the zinc spark employed by Warburg in his early work gave[24] at 2540A a thousand-fold the intensity of a mercury vapor lamp.

Lifschitz[25] obtained intense light and high temperatures by sparking between the whole length of a pair of electrodes. Ogg, Leighton and Bergstrom[26] describe a spark gap (Figure 10) in which the spark passed between the tapered edges of two rotating disks of cobalt or cadmium, A,A′ mounted on hollow shafts, B,B′, through which cooling water was circulated. To provide insulation, the cooling water circuit was broken by sprinklers. The frames holding the shafts were movable, so that the gap length, usually about 1 cm., could be adjusted by the screws I,I′.

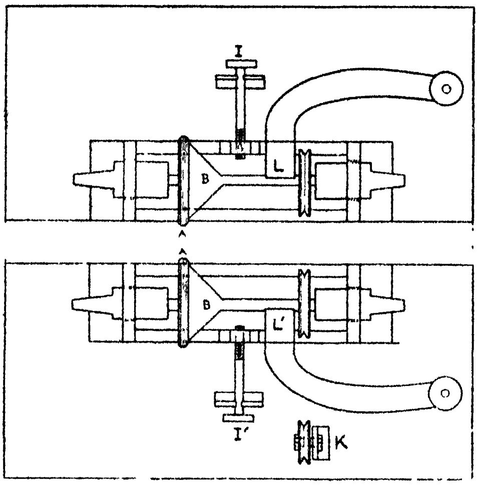

FIGURE 10.

Spark Gap with Rotating Water-cooled Electrodes (Ogg, Leighton and Bergstrom, *Journal American Chemical Society*).

The shafts were belt-driven in opposite directions at several hundred r.p.m. by a ¼ h.p. motor. Electrical contact was made through heavy carbon brushes L,L′, connected to the terminals of a 0.010 mfd. oil-immersed condenser across the secondary of a 5 kw. x-ray transformer. By this means one to two discharges per half cycle were obtained across the gap. A hose (attached to a vacuum line) mounted close behind the spark drew off objectionable fumes. The gap was readily demountable for cleaning and oiling of the bearing and interchange of electrode disks.[27]

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[23] Forbes, G. S., *J. Phys Chem*, **32**, 485 (1928).

[24] Warburg, E., *Sitzb. Preuss Akad. Wiss*, 746 (1911), 216 (1912), 314 (1916)

[25] Lifschitz, S., German P. 524,877, March 26, 1926, *Chem Abs.*, **25**, 4189 (1931)

[26] Ogg, R. A, Jr, Leighton, P. A., and Bergstrom, F. W, *J Am. Chem. Soc.*, **55**, 1754 (1933). See also van der Lingen, J. S., *S African J. Sci.*, **33**, 197 (1937)

PHOTOCHEMICAL REACTIONS IN GASES SURROUNDING SPARKS

Jolibois, Lefebvre and Montagne[28] state, from observations on the change in pressure, that carbon dioxide at pressures between 0.3 and 20 mm. of mercury when subjected to a spark discharge, is decomposed into carbon monoxide and oxygen. A limiting dissociation of 90 per cent is attained. About 20 per cent of the energy of the first spark is converted into chemical energy; the remainder is dissipated. The decomposition increases with the voltage and is influenced by the size and shape of the containing vessel and the position of the electrodes. The yield rises to a maximum and falls as the capacity of the circuit decreases, and for a given capacity the maximum yield falls off slightly as the pressure increases.

Methane, under a pressure of 1 to 11 mm., was transformed into ethylene and hydrogen[29] under a spark discharge. Apparently little industrial use has been made of the radiations from a spark gap, although its use as a means of generating a bleaching gas for flour and cornmeal has been patented.[30]

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[27] For other spark apparati, see Henri, V., *Compt. rend.*, **157,** 126 (1913); Kuhn, W., *Ibid.*, **178,** 708 (1924).

[28] Jolibois, P., Lefebvre, H., and Montagne, P., *Compt. rend.*, **182,** 1026 (1926), **184,** 522 (1927). General discussions are due to Lefebvre, H., *Chimie et Industrie*, Special Number, June, 427, 1933, and to Jolibois, P., *Ber.*, **71A,** 73 (1938).

[29] Montagne, P., *Compt. rend.*, **194,** 1490 (1932).

[30] Stuff, F., German P. 510,419, Dec. 23, 1927, *Chem. Abs.*, **25,** 1008 (1931), German P. 518,201, June 28, 1929, *Chem. Abs.*, **25,** 2377 (1931), German P. 521,360, Dec. 25, 1929; *Chem. Abs.*, **25,** 2651 (1931), Brabender, C. W., *Mehlprobleme*, **1,** 6 (1932).

Chapter 5

The Open Arc

Arcs may be produced between electrodes that are open to the air or enclosed in a vessel of glass or quartz. In the case of the enclosed arcs, the pressure may be very low or it may be atmospheric or greater.

In most arcs, the use of very high starting potentials is obviated by bringing the electrodes into contact (closed circuit) and then drawing them apart. The resistance offered to the passage of the current heats the electrodes to a temperature such that, when drawn apart, they produce vapors of the electrode material. The latter carry a bright discharge across the intervening space. The arc discharge, which may carry many amperes, is very hot and the electrodes become brightly luminous.

The mechanical features of the arc vary with the use for which it is intended, as commercial illumination, spectrographic analysis, as an ultraviolet source for conducting photochemical reactions or for fluorescence studies. An arc which will emit ultraviolet energy strongly may be prepared by employing an iron rod and a carbon rod for the two poles. Also, two iron rods may be used. These poles are cooled by means of heavy brass or copper sleeves, which may be moved along the iron rods as the latter are consumed. Thus, the upper pole (negative) may be an iron rod about one-quarter inch in diameter. This rod is surrounded by a movable but well-fitted sleeve of copper about one inch in diameter with hollowed end. One pole should be adjusted vertically. In preparing the arc, a bead of molten metal is developed in the dished end of the lower electrode. The upper electrode is well cooled and the arc is maintained very steadily between the bead of molten iron and the upper solid electrode. Luckiesh has had such an arc operate at a rather high current density for thirty minutes without any adjustment.

ELECTRICAL CHARACTERISTICS

Metallic arcs in general will not burn on alternating current. The carbon (but not the graphite) arc will, however, burn on alternating currents at potentials as low as 80 volts. On direct current, the carbon arc burns with voltages as low as 37. Iron and copper arcs require higher voltages, 80 and 90 at least. Arcs between electrodes of materials with good thermal conductivity tend to extinguish readily.

A number of observers have developed empirical equations for the relation between the length of the arc and the voltage, or between the energy, current, voltage and arc length.[1] The Ayrton equation for the carbon arc, $V=A+B/I$, has been made more accurate and more general by Nottingham by raising the current I to a power n. A and B are constants depending upon the arc length and pressure. The equation applies if the anode is very hot. The power *n* is a constant dependent upon the boiling or sublimation point of the metal of the anode. It is 0.67 for copper, 1.38 for tungsten, and approximately 1 for carbon, the latter accounting for the success of the Ayrton equation. The dependence of this constant upon the nature of the anode led Myer[2] to suggest that the anode may have a more important role in the arc mechanism than most theories of the arc discharge would imply. Alterthum and Ewest[3] believe that the anode exerts an important effect over the entire discharge, for by preheating the anode, the striking and operating voltage of the arc can be greatly reduced. Hagenbach and Langbein[4] stated that in normal arcs, the anode is boiling during discharge. The form of the equation also shows that an increase in the current is accompanied by a drop in the potential, showing that Ohm's law does not apply to conduction in the arc.

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[1] Ayrton, Mrs. H., "The Electric Arc," Chapter IV, New York, van Nostrand, 1902; Malcolm, H. W., and Simon, H. T., *Physik Z.*, **8**, 471 (1907); Steinmetz, C. P., *Trans Am Inst Elec. Eng*, 802 (1906); Bramhall, E. H, *Phil. Mag.*, **13**, 682 (1932); Nottingham, W. B., *Am Inst. Elec. Eng.*, **42**, 12 (1923); *Phys. Rev.*, **28**, 764 (1926); Anderson, S. H., and Kretchmar, G A, *Phys. Rev.*, **26**, 33 (1925); Doan, G. F., and Myer, J. L., *Elec. Eng.*, Sept., 1932; Sommer, J. J., and Bott, J., *Physik. Z.*, **34**, 324 (1933), Kotecki, A., *Acta Phys. Polon*, **4**, 113 (1935).

With heavy currents, above ten amperes, the voltage approaches the limiting value *A*. The pressure of the gas is also a factor. The required potential increases continuously with the pressure; the values at ten atmospheres may be 15 to 20 volts greater than at one atmosphere.[5]

The theory of the mechanism of the arc discharge has lagged somewhat behind practice. The development of the quartz mercury-vapor arc was based to a large extent upon empirical observations and trial and error methods. The theory of the open arc is still the subject of many controversial statements.[6] The development of arc theory may be approached through a consideration of the phenomena of glow discharge at low pressures, which has been summarized by Dushman,[7] Langmuir,[8] and by Pirani.[9]

The various easily recognizable regions of the glow discharge are also found in arcs through gases at low pressures but are masked in the high-pressure or open arc. The theories of the latter are, however, based upon the application of principles derived from the study of the glow discharge. The fundamental processes of the emission of electrons from hot cathodes, the liberation of electrons by thermal ionization of atoms and molecules of gases, the acceleration of electrons in potential fields and the results of impact of electrons with atoms and molecules leading to excitation and the emission of radiations, all are encountered in high-pressure or open arcs as they are in the glow discharge. Complications in study of open arcs arise from such effects as the high temperature glow of the electrodes, vaporization and sputtering of the electrodes and combustion in the flame of the arc.

Thermionic emission of electrons from the cathode, heated by positive ion bombardment, has been believed adequate to account for the current densities in the tungsten arc or carbon arc.[10] Although the temperatures of the copper, iron and nickel arc cathodes have been found to lie near the boiling points of these metals[11] such temperatures are said to be too low to produce sufficient electrons to give the observed current densities.[12] Furthermore, so-called "cold cathode" arcs are known to be obtainable.[13] Slepian reported that the arc current to the cathode may be carried by positive ions resulting from thermal ionization of the gas, in accordance with the Saha equation. The necessary temperatures of 6000 to 7000° were assumed to exist in a thin layer of gas next to the cathode. Langmuir[14] introduced a different theory in which electrons are assumed to be drawn from the cathode by a very intense electrostatic field near the cathode surface set up by a positive space-charge sheath, a view further developed by Mackeown and Compton.[15]

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[2] Myer, J. L., *Trans. Am. Inst Elec. Eng.*, **52,** 250 (1933).

[3] Alterthum, H., and Ewest, H , *Z. tech. Physik*, **9,** 221 (1928).

[4] Hagenbach, A., and Langbein, K , *Arch. Sci.*, **1,** 48 (1919).

[5] See also Anderson, S H., *Phys. Rev*, **29,** 750 (1927).

[6] For a detailed earlier account, see Compton, K. T., *J. Am. Inst. Elec. Eng* , **46,** 868, 1192 (1927)

[7] Dushman, S , *Elec. Eng.*, **53,** 1204, 1283 (1934).

[8] Langmuir, I., *Gen. Electric Rev* , **38,** 514 (1935).

[9] Pirani, M., *Z. angew. Chem.*, **44,** 395 (1931); Lex, E , Pirani, M., and Rompe, R., *Naturwiss.*, **23,** 393 (1935) See also for greater details, Langmuir, I., and Compton, K. T., *Rev. Mod. Physics*, **3,** 191 (1931); Found, C. G , and Forney, J. D., *J. Am Inst. Elec. Eng.*, **47,** 747, 855 (1928); Kirschstein, B., and Koppelmann, F., *Z. tech. Physik.*, **15,** 604 (1934), and the books, Kohler, W., and Rompe, R., "Die Elektrischen Leuchtrohre," Vieweg, 1933; Seeliger, R., "Physik der Gasentladungen," Leipzig, Barth, 1927; Darrow, K. K., "Electrical Phenomena in Gases," Baltimore, Williams and Wilkins, 1932.

[10] Nottingham, W. B., *J. Frank. Inst.*, **205,** 811 (1928); Mason, R. C., *Phys. Rev.*, **38,** 427 (1931).

Much work has been done upon the relation between the potential drop at the cathode and the ionization potentials of the gases or vapors which emit radiations when the molecules or atoms are struck by the electrons. Electron densities have also been related to the intensities of lines or bands emitted.[16] Nottingham states the cathode drop of 20 volts in the copper arc to correspond with the second ionization potential of copper vapor. In the cadmium arc, the drop, 8.4 volts, agrees with the ionization potential of cadmium. In the thallium arc, the drop was slightly higher than 6.08 volts, the ionization potential of thallium. In the carbon arc, the cathode fall of 5 volts agreed fairly well with the ionization potential (4.4 volts) of the cyanogen molecule. It may be noted, however, that others report the cathode drop of the carbon arc as 9 volts. That the electrons in the arc plasma could have the necessary velocities to give the required excitation energies implies that the electrons must have a greater velocity of agitation than might be expected from the potential gradient between collisions. The velocity of agitation of the electrons implies an "electron temperature" By the use of the Langmuir probe methods, Nottingham[17] found this temperature to be 6000° for the cadmium arc, 8000° for the thallium arc and 19,000° for the copper arc, or sufficient to account for the observed intensities of the emitted lines.[18]

In the course of his work on arc temperatures, Nottingham[19] developed a photographic method for finding the area of the hot spot on the cathode from which the arc passes. This area appeared to increase in proportion to the total current, so that the current density remained constant In the arc itself, a magnetic field due to the current tends to concentrate the discharge about a longitudinal axis in its center.[20]

The vapors distilled from metallic arcs have been studied by Rayleigh[21] and by Berkey and Mason.[22] Matter is lost from the cathode of an iron arc. The decrease in weight of the latter is not proportional to the current alone, but depends

[11] Hagenbach, A, and Langbein, K, *Arch Gen.*, **461,** 329 (1918), Tanberg, R, and Berkey, W. E., *Phys. Rev*, **38,** 296 (1931).

[12] Slepian, J., *Phys Rev.*, **27,** 407 (1926); Seeliger, R, *Physik Z*, **27,** 22 (1926); **31,** 691 (1930).

[13] Nicol, J, *Proc. Roy Soc*, **82A,** 29 (1909), Stolt, H., *Z Physik*, **26,** 95 (1924).

[14] Langmuir, I., *Gen. Elec Rev.*, **26,** 735 (1923), *Z Physik*, **46,** 282 (1927).

[15] Mackeown, S S, and Compton, K T, *J Am Inst Elec. Eng*, **46,** 1192 (1927) See, however, Slepian, J., and Haverstick, E J., *Phys Rev*, **33,** 52 (1929), and Mason, R. C, *Ibid*, **38,** 427 (1931).

[16] See for the copper arc measurements, Bramhall, E H, *Phil Mag*, **13,** 682 (1932); Ornstein, L. S, and Vermeulen, D, *Z. Physik*, **70,** 564 (1931); Schmidt, R W., *Z. Physik*, **106,** 35 (1937); Robertson, R. M, *Phys Rev.*, **53,** 578 (1938).

[17] Nottingham, W B, *J Frank Inst.*, **206,** July, 1928; **207,** March, 1929; **208,** 192 (1929)

[18] See, however, Bramhall, E. H, *Phil Mag*, **13,** 682 (1932). These relations have been discussed more exactly in the positive columns of low pressure gas discharges.

[19] Nottingham, W. B, *J. Frank. Inst*, **205,** 811 (1928).

[20] Northrup, E. F., *Phys Rev*, **24,** 474 (1907).

[21] Rayleigh, Lord, *Proc. Roy Soc*, **112A,** 14 (1926).

[22] Berkey, W. E, and Mason, R. C., *Phys. Rev.*, **38,** 943, 1783 (1931).

also upon the cooling of the cathode.[23] The whole surface adjacent to the bright spot contributes to the loss. This vaporization of the electrodes makes their nature of particular importance in determining the potential difference across an arc of given length, and in obtaining the constants in the modified Ayrton equation. The transport of luminous material in the arc has been studied by measuring the variations in the intensities of the spectral lines in different portions of the arc,[24] as well as by other methods.[25] Very high velocities have been observed.[26]

SPECTROGRAPHIC ARCS [26a]

An arc between iron electrodes generally is employed in spectroscopy. Baly[27] used a horizontal arc with the iron poles mechanically rotated in opposite directions. The arc was stated to be capable of giving long exposures. This was a modification of a device of Crew and Tatnall[28] in which one electrode comprised a rapidly revolving disk mounted on the armature of a motor and carrying on its periphery small pieces of the metal whose spectrum was to be observed. The other electrode was a rod of the same metal mounted on a fine-cut screw so that the position of the electrode could be accurately adjusted.[29]

The Pfund arc,[30] used as a steady source for the measurements of wave-lengths of the iron arc, is vertically mounted. In operation, the iron arc makes a transition from a high voltage stage to a low voltage stage with currents of about one ampere. Cady and Arnold[31] find the excess potential in the high voltage stage to lie in the anode fall. The iron arc burns at low voltages in impure argon, helium or neon, but cannot be struck in these gases if the latter are rigidly purified.[32]

An enclosed iron arc described as a convenient source for the standardization of spectral lines[33] emits a discharge in an inert gas. The latter is maintained at atmospheric pressure. In this manner one electrode is heated to a temperature sufficient to provide enough metal vapor to yield the iron spectrum At least one electrode is compacted of sintered pure iron or iron compounds and contains an electron-emitting substance such as barium or calcium oxide. Titanium, tungsten, molybdenum and chromium must be absent to prevent confusion in reading the spectrum. A window for transmitting the radiations is placed on a tubular extension of the bulb.

Data on exact wave-lengths of the standard lines of the iron arc have been

[23] Schmick, H, and Seeliger, R, *Physik Z*, **29**, 864 (1928) See also Laudet, G, *Compt. rend*, **192**, 202 (1931), and Kirschstein, B, *Wiss Veroffent. Siemens-Werken*, **16**, 69, 72 (1937), *Chem. Abs*, **31**, 7341 (1937), **32**, 2034 (1938)

[24] Ornstein, L S, and Koopmans, T, *Proc Acad Sci Amsterdam*, **34**, 1099 (1931), *Chem Abs*, **26**, 4755 (1932)

[25] Tanberg, R, *Phys Rev*, **35**, 1080 (1930)

[26] See, e.g, Slepian, J., and Mason, R. C, *Phys Rev.*, **37**, 779 (1931), Compton, K. T, *Ibid*, **36**, 706 (1930).

[26a] For a summary of recent theory, Rollwagen *Spectrochem Acta*, **1**, 66 (1939)

[27] Baly, E. C. C, "Spectroscopy," Vol **2**, p 91, London, Longmans Green and Co, 1927

[28] Crew, H, and Tatnall, R, *Phil Mag*, **38**, 379 (1894).

[29] See also Neuhaus, C J, *Am Soc Testing Materials*, Preprint No. 51 (1938), *Chem. Abs*, **32**, 6105 (1938)

[30] Pfund, A H, *Astrophys J*, **27**, 296 (1908).

[31] Cady, W G, and Arnold, H D, *Physik Z* **8**, 890 (1907)

[32] Doan, G E, and Myer, J I, *Phys Rev*, **40**, 36 (1932)

[33] British P. 401,509, Nov 16, 1933 (Patent Treuhand Gesellschaft fur elektrische Gluhlampen, assigned to General Electric Co, Ltd), see also Pirani, M, and Rompe, R., *Z. tech. Physik*, **13**, 134 (1932).

reported by Babcock[34] and by Burns and Walters,[35] with particular reference to the vacuum arc.*

ULTRAVIOLET SOURCES FOR PHOTOCHEMICAL PROCESSES

Temperatures and energies emitted in small tungsten arcs have been studied by de Groot.[38] Moore[39] employs electrodes of an alloy composed essentially of tungsten with 1-5 per cent of titanium and 0.25-2.0 per cent of chromium. The tungsten arc between rods of 6.4 mm. diameter is rather unsteady and hard to keep in focus because of the formation of a crust of oxide around the electrode. It is weak in rays of less than 2300A, from which wave-length there is a gradual increase in intensity to a maximum at 4500A.

Arcs carrying 6 amperes between 12 mm. nickel rods are said to provide quiet-burning sources of ultraviolet, emitting strongly at 2300 and at 3500A.[40] Macdonald[41] produces ultraviolet rays by means of an arc created in a vacuum from electrodes of gold alloyed with copper or silver. Nagaoka and Suguira[42] described an arc in which the cathode was a carbon rod coated with barium or strontium oxide, the rod being sheathed in a silica tube. Various metals or salts in a similar silica tube served as anode. The arc operated in a vacuum and at 1500 volts produced rays which penetrated aluminum foil. Vaporization of the anode metal, short life of the arc, and the necessity of cooling the system and pumping to maintain vacuum were among the reported disadvantages of this arc. Albers[43] described an apparatus for maintaining an enclosed beryllium arc in any atmosphere at reduced or elevated pressures.

THE CARBON ARC

The carbon arc was discovered by Sir Humphry Davy, between 1802 and 1808 He employed a 2000-plate voltaic battery as source of current and obtained an arc three inches long. The development of carbon arcs has followed two chief paths. One is the design of steady, very brilliant arcs for motion-picture projection or for air-port illumination. The second has been concerned with methods for altering the distribution of the intensity of the radiation within various spectral regions to meet special demands of industrial photochemistry. Also, the carbon arc is utilized for therapeutic purposes. Much of the progress has been due to alterations in the carbon electrodes.

An early advance consisted in the introduction of a central core of a soft, neutral composition, which stabilizes the arc stream and prevents the latter from shifting about the rim of the crater. Coating the carbons with copper or other metals lessens overheating. The light from either the solid or the neutral-cored carbon arc (on direct current) comes almost entirely from the crater of the positive carbon, little being derived from the arc stream or the tip of the negative carbon. With alternating current, there are two craters of light, but the brilliancy and efficiency are somewhat less than that secured with direct current.

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* What is known as the pole-effect is a slight difference in the wave-lengths of many lines when the arc is examined near the poles or at the center.[36] The pole-effect does not affect ordinary analytical methods and is of importance only in precise spectrographic work. In some instances, revolving electrodes may be employed.[37]

[34] Babcock, H. D., *Astrophys. J.*, **67**, 240 (1928).

[35] Burns, K., and Walters, F. M., Jr., *Pub. Allegheny Observatory*, **6**, 159 (1929); *Chem. Abs.*, **23**, 4886 (1929)

[36] St. John, C. E., and Babcock, H. D., *Astrophys J.*, **42**, 231 (1915).

[37] Sventitskii, N S, *Zavodskaya Lab.*, **6**, 325 (1937); *Chem. Abs*, **31**, 7762 (1937).

[38] de Groot, W., *Physica*, **5**, 121, 234 (1925), *Chem. Abs*, **19**, 2449, 3215 (1925). For line measurements, see Laun, D D., *Phys Rev.*, **48**, 572 (1935)

[39] Moore, W. G., U S. P. 1,872,322, Aug 16, 1932; *Chem Abs*, **26**, 5857 (1932). Note also Blake, G G., British P, 279,680, Jan. 4, 1927

[40] Coblentz, W. W., Dorcas, M, and Hughes, C W, *Sci Papers, Bureau of Standards*, **21**, No 539, p. 547 (1926).

[41] Macdonald, R. F., British P 206,588, Aug. 9, 1922; *Chem Abs* **18**, 1090 (1924).

[42] Nagaoka, H., and Suguira, Y, *Astrophys. J*, **57**, 86 (1923).

[43] Albers, V. M, *J Opt. Soc. Am*, **19**, 146 (1929).

There have been developments in the application of refractory coatings. Thus, the electrodes may be placed in a silica tube and heated to 700° in a current of silicon tetrafluoride at a pressure slightly above atmospheric to form a non-oxidizable coating which retards combustion.[44] Other coatings of silicon or tungsten carbides[45] or of sprayed chromium on the carbon[46] have been described. In some instances, the carbon first is covered with silvered copper, and the whole sprayed with chromium. The use of a cellulose lacquer coating to prevent the absorption of water on the carbon, which causes flickering, has been proposed by Wilson.[47] As the arc passes, the positive terminal becomes hollowed out to a crater, while the negative terminal remains pointed. According to Griffith, Taylor and Jack[48] the flame of the arc contributes most of the radiation which is effective therapeutically. The efficiency of the arc increases to a limiting value with flame length, above which the efficiency is independent of flame length. The ultraviolet emission is a function of the watts consumed in the flame of the arc.

A high intensity carbon arc, intended for motion picture projection in large theatres, comprises cored $\frac{8}{16}$ mm. positive carbons (without metallic coatings) and smaller copper-coated negative carbons.[49] The arc is operated with a horizontal positive carbon, continuously rotated to maintain a well-formed crater. The cathode is placed at an angle 40-60° below the horizontal. Arc currents of 60 to 190 amperes are employed at 45 to 90 volts, d.c. The spectral energy distribution is said to be similar to that of sunlight. The crater furnishes 70 per cent of the light, the remainder coming from the tail-flame The color and brilliancy of the light indicate a temperature of 5500°C. Since this is higher than the vaporization temperature of carbon, the source must be other than the solid tip of incandescent carbon. Alternating current high intensity arcs have been developed. High intensity carbons usually are cored with cerium fluoride or some similar material. The very high current densities require the use of oxides, fluorides, etc., in a central rod, embedded in the carbon.[50] Only difficultly vaporizable substances may be used in the core. Alkalies must be avoided as they are detrimental to the brilliancy of the crater.[51] Beck has described the construction of a negative electrode for high intensity arcs.[52]

Temperatures in the arc may be estimated by a study of the intensities of band spectra.[53] Ornstein and Brinkman [54] concluded from the intensity of the cyanogen bands at 3884 and 4216A, that the violet kernel of the carbon arc shows a temperature of 6500°K. Lower temperatures of 2950 to 3600° were obtained when the bands of AlO were produced by filling the anode cup with alumina and carbon. Other results indicated the arc gases to have temperatures exceeding those of the electrodes, showing that the high temperature of the gas plays an essential role in the discharge mechanism.[55] By a method based upon the reflectivity of carbon, Warmuth [56] calculates the temperature of the positive crater to be 3740°C. Chaney, Hamister and Glass [57] find the temperature of the positive crater to approach as a limit the sublimation point of pure crystalline graphite. They state the maximum brightness temperature of the carbon crater is probably 3810°K or 40° higher than that found by Waidner and Burgess. The true crater temperature they believe to be between 3925 and 3970°K.

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[44] Singleton, W., and Hare, A , British P. 248,167, March 17, 1925 (General Electric Co., Ltd.).

[45] I. G. Farbenindustrie, German P. 578,501, June 14, 1933.

[46] C. H Champion and Co , Ltd , and Champion, C. H., British P. 406,434, March 1, 1934.

[47] Wilson, W. N., British P. 395,073, July 13, 1933.

[48] Griffith, H. D., Taylor, J. S., and Jack, J. M., *Brit. J. Radiology*, **23**, 203 (1927); *Chem. Abs.*, **21**, 3830 (1927).

[49] Kalb, W. C , *Elec. Eng.*, **53**, 1173 (1934); **56**, 319 (1937). See also Bassett, P. R , *Trans. Am. Electrochem. Soc* , **44**, 153 (1923). The toxicity of the fumes from such arcs appears to be due primarily to nitric oxide, carbon monoxide being negligible, according to MacQuiddy, E L., Tollman, J. P., LaTowsky, L. W., and Bayliss, M , *J. Ind. Hyg. Toxicol.*, **20**, 297, 312 (1938); Coltman, R. W., *Ibid.*, **20**, 289 (1938).

[50] Orne, S. W., U. S. P. 1,867,524, July 12, 1932; *Chem. Abs.*, **26**, 4544 (1932); Dorcas, M., U. S. P. 1,920,921, Aug. 1, 1933; *Chem. Abs.*, **27**, 4746 (1933).

[51] British P. 285,424, June 19, 1929 (Compagnie Lorraine de Charbons pour l'Electricité); see also U S. P. 1,952,810, March 27, 1934; *Chem. Abs.*, **28**, 3317 (1934), and British P. 475,252, Nov. 16, 1937; *Chem. Abs.*, **32**, 3280 (1938).

[52] Beck, H., U. S. P. 1,991,998, Feb. 19, 1935.

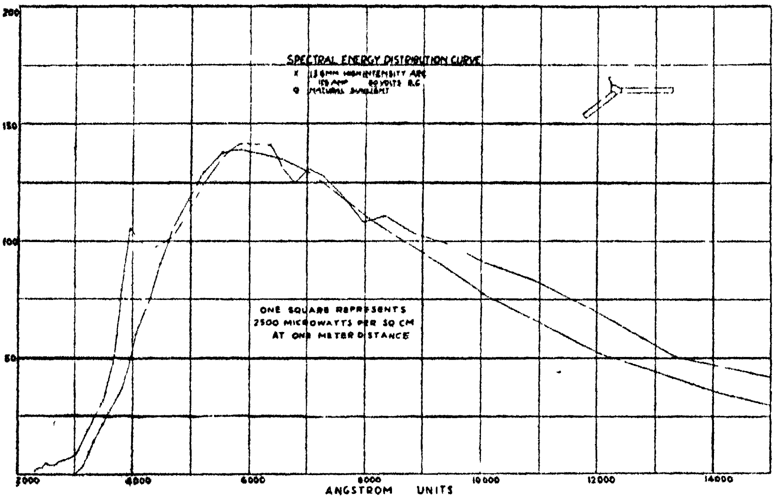

FIGURE 11. Spectral Energy Distribution Curves of Sunlight and High-intensity Carbon Arc (Greider, *Industrial and Engineering Chemistry*)

Ryde [58] found that in arcs with a positive carbon cored with calcium fluoride and operated at current densities greater than the limiting current densities for ordinary carbons, a bright central core develops in the arc stream. In the central core, the spectra of neutral carbon, nitrogen and oxygen, the Balmer series of hydrogen and some argon lines are excited. Of the two chief band systems, *i.e.*, the Swan bands and the cyanogen bands, the former are strongly excited close to and inside the positive carbon, but do not appear at all in the arc stream under normal conditions. The origin of the cyanogen bands is well established, since they are absent when the arc is operated in a gas free from nitrogen. The Swan bands appear to be formed by C_2.[59] An increase in current rapidly increases the intensity of the cyanogen bands.

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[53] v. Engel, A., and Steenbeck, M., [*Naturwiss.*, **19,** 212 (1931), *Chem. Abs.*, **25,** 2357 (1931)], use the absorption of x-rays.

[54] Ornstein, L. S., and Brinkman, H., *Naturwiss.*, **19,** 462 (1931); *Proc. Acad. Sci. Amsterdam*, **34,** 33, 498 (1931); *Chem. Abs.*, **25,** 3567, 5842 (1931).

[55] Ornstein, L. S., Brinkman, H., and Vermeulen, D., *Proc. Amsterdam*, **34,** 764 (1931), Ornstein, L. S., *Physik. Z.*, **32,** 517 (1931); Ornstein, L. S., Brinkman, H., and Beunes, A., *Z. Physik*, **77,** 72 (1932); Mason, R. C., *Physica*, **5,** 777 (1938); *Chem. Abs.*, **32,** 8364 (1938). For determinations by other methods see Hörmann, H., *Z. Physik*, **97,** 539 (1935). Lochte-Holtgreven, W., and Maecker, H., [*Z. Physik*, **105,** 1 (1937)] raise the values from cyanogen bands to 7600° for the normal and to as high as 8700° for an over-run arc. See also Khlebnikova, L. Y., *J. Exptl. Theor. Phys. (U.S.S.R.)*, **7,** 1220 (1937); *Chem. Abs.*, **33,** 4866 (1939); Khramova, E. F., *J. Exptl. Theor. Phys. (U.S.S.R.)*, **8,** 176 (1938); *Chem. Abs.*, **33,** 4866 (1939)

[56] Warmuth, K., *Wiss. Veröffentlich. Siemens-Konz.*, **7,** 307 (1928); *Chem. Abs.*, **23,** 316 (1929).

[57] Chaney, N. K., Hamister, V. C., and Glass, S. W., *Trans. Electrochem. Soc.*, **67,** 107 (1935).

[58] Ryde, J. W., *Proc. Roy. Soc. London*, **117A,** 164 (1927).

The distribution of energy in the carbon arc operated under various conditions has been determined by Greider,[60] who employed a quartz monochromator for the region between 2300 and 7000A and an infrared spectroradiometer between 6000 and 18000A. The relative energy distribution curves were converted into absolute energy unit curves by a method involving the use of a galvanometer and thermopile.[61] In the curves reproduced in Figures 11 and 12, unit areas represent unit amounts of energy, so that the intensity between any two wave-length limits may be estimated by measuring the corresponding area under the curve.

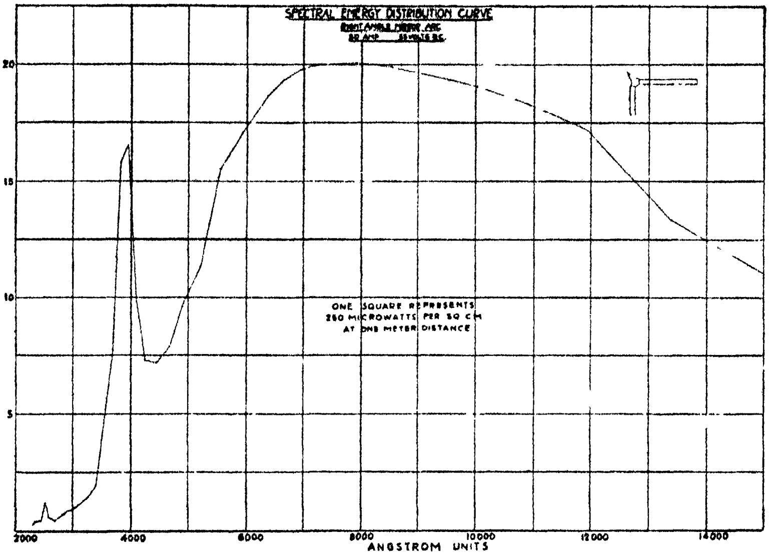

FIGURE 12. Spectral Energy Distribution Curves of Plain-carbon Arc, Burned under Low-intensity Conditions (Greider, *Industrial and Engineering Chemistry*).

Figure 11 compares the energy distribution from a 13.6 mm. high-intensity arc operated at 125 amperes and 80 volts d.c. with that of normal sunlight. Each square represents 2500 microwatts per sq cm. at a distance of one meter. The agreement is quite remarkable, the chief difference being in the greater output by the arc of radiations shorter than about 4500A. The spectrum also extends to a shorter wave-length limit, although this forms but an insignificant fraction of the total radiation from the arc.

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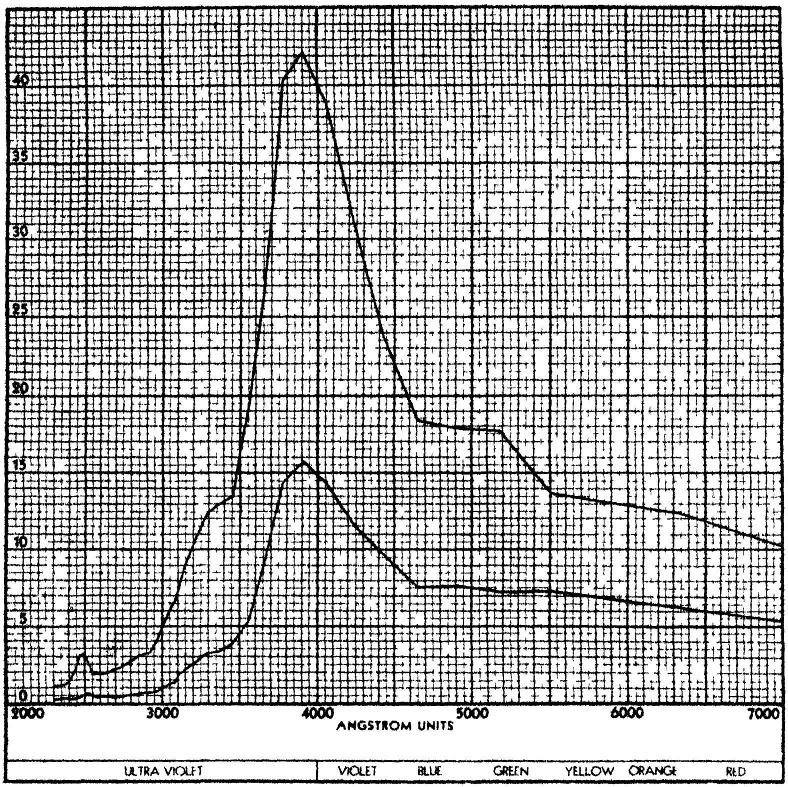
[59] Johnson, R. C, *Nature*, **116**, 539 (1925); Johnson, R. C., and Asundi, R K., *Proc. Roy. Soc, London*, **124A**, 668 (1929)

[60] Greider, C. E., *Ind. Eng Chem.*, **23**, 508 (1931), for a discussion of the methods employed in such measurements, see Chapter 7.

[61] Greider, C. E, and Downes, A. C., *Trans Illum. Eng Soc*, **25**, 378 (1930), **27**, 637 (1932). See also Mandel'shtam, S L., *Compt rend acad. sci U R S.S.*, **18**, 559 (1938).

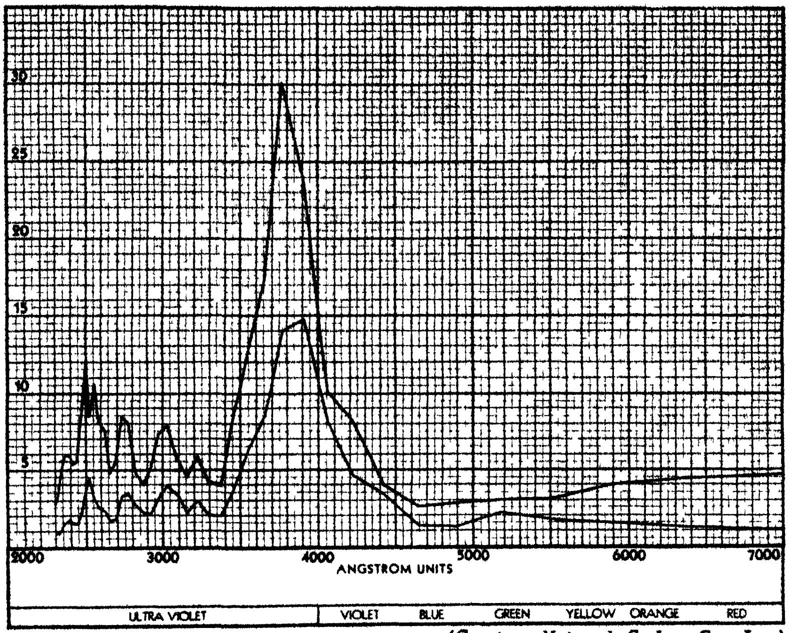
The energy distribution of the plain carbon arc with poles at right angles and carrying 30 amperes at 55 volts is shown in Figure 12 in which each square represents but one-tenth of the energy of the previous figure. This arc burns at a lower temperature, so that the total intensity is lower, and the intensity maximum occurs at a longer wave-length. There appears also a larger amount of the line or band spectrum from the arc stream, giving peaks at 2500 and 3900A. When a plain vertical carbon arc is utilized, there is found to be relatively less continuous radiation from the craters. Also the maximum intensity lies much farther toward the infrared than with high intensity carbons. This flame carbon arc may be made into a versatile source of radiation by the addition to the electrode of various substances, which may be vaporized into the arc. The added materials are either distributed throughout the carbon or, more commonly, are concentrated into a central core.



(Courtesy National Carbon Co., Inc.)

FIGURE 13. Spectral Energy Distribution of Sunshine Carbons.

Figure 13 gives the energy distribution of Sunshine carbons which contain cerium in the core. As compared with the neutral core arc, there is a marked increase of energy in the ultraviolet, increasing gradually in intensity from about 2900 to 4000A. There is a fairly uniform intensity at a much lower level, from about 4500 to 8000A, due to lines so closely packed together as to yield a nearly continuous spectrum. Beyond about 8000A the intensity falls off rapidly, practically all radiation in this area being that from the incandescent poles. Such arcs are especially suitable for photography and photoengraving. Reactions believed to occur within the arc stream or hot electrodes of the cerium carbons have been discussed by Bassett.[62] These carbons are also suitable for therapeutic arcs in which it is desired to imitate sunlight. The lower and upper curves in Figure 13 refer to the output of the arcs operated with 30 and 60 amperes, respectively. Figures 14, 15, 16, 17, and 18 give similar data for various other therapeutic carbons ("B," "C," "E," "K" and "U" are the trade designations). In each case the output increases much more rapidly than the rate of current increase. Up to about 30 amperes, the output is approximately equal to the square of the current, but at higher currents the rate of output decreases. The "B" carbons contain iron and yield light similar in general distribution to that of the mercury arc.



(Courtesy National Carbon Co, Inc)

FIGURE 14. Spectral Energy Distribution of Therapeutic B Carbons.

The "C" carbons contain in the core a mixture of metals including iron, nickel and aluminum. Dorcas[63] has described the preparation of these electrodes. A hollow shell tube of carbon is formed and baked at 1400°C. Into the tube is then forced the core and the whole heated. These carbons give a series of groups of very intense lines in the ultraviolet, with but a relatively low intensity of energy in the visible region. The infrared radiation follows the general shape of the curve for the incandescence of carbon craters, but is relatively low in intensity. The "C" carbons are used for ultraviolet therapy as they have an even distribution of radiation through the physiologically active range. A 30-ampere "C" carbon arc at 50 volts, a c, is said to give two to seven times as much biologically active ultraviolet energy as do mercury arcs. The "C" carbon is particularly strong in the zone

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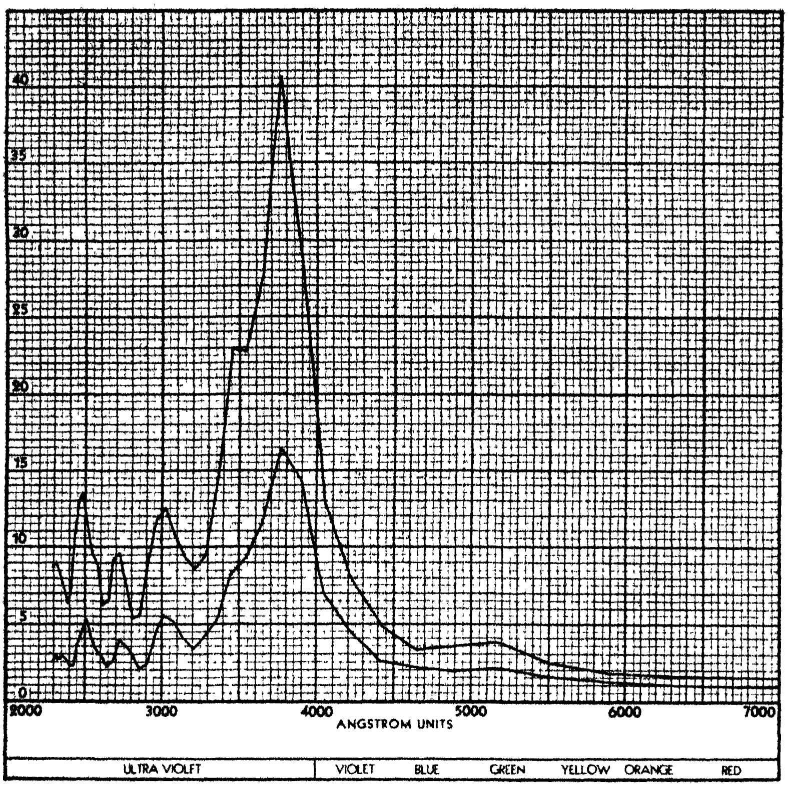
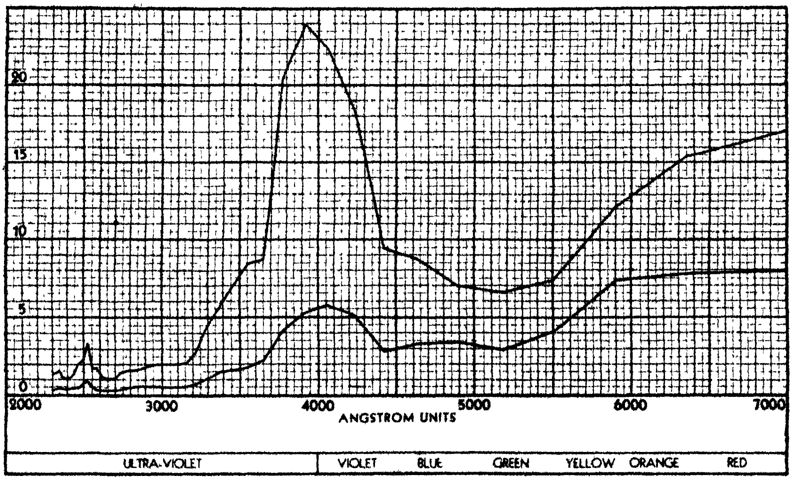
[62] Bassett, P. R., *Trans Electrochem. Soc*, **44**, 153 (1923).

[63] Dorcas, M. J., U. S P. 1,862,300, June 7, 1932.



(Courtesy National Carbon Co., Inc.)

FIGURE 15. Spectral Energy Distribution of Therapeutic C Carbons.

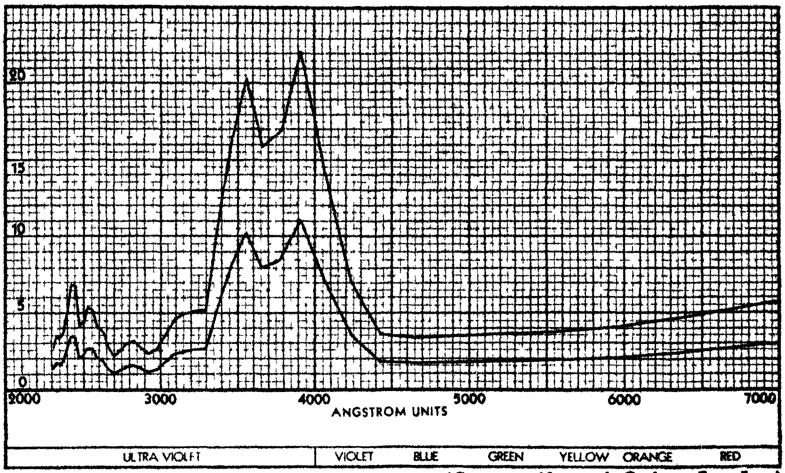


(Courtesy National Carbon Co., Inc.)

FIGURE 16. Spectral Energy Distribution of Therapeutic E Carbons.

of antirachitic radiation (2700 to 3000A) and is the strongest of all therapeutic carbons of the National Carbon Co. series in the tan-producing zone from 3000 to 3200A.

To secure particular energy distributions in the ultraviolet wires of zinc or aluminum may be embedded in holes bored in the carbon. Copper and cobalt usually are added in powder form to the carbon Cobalt ("K" carbons) gives a very high intensity near 2400A and a peak near 3600A, with a low intensity in the visible and infrared in comparison with the plain carbon arc. In absolute units the energy is not far different at 9000A and at the 2400A peak. This carbon is said to simulate in effects the Kromayer mercury arc. (See page 126)



(Courtesy National Carbon Co., Inc.)

FIGURE 17. Spectral Energy Distribution of Therapeutic K Carbons.

To secure particularly the region 2800 to 3100A, Greider[64] employs about equal quantities of iron, chromium, manganese and titanium in the core of the carbon. Arcs with calcium or strontium compounds in the core have relatively little energy in the ultraviolet. The strontium arc ("E" carbons) is used in infrared therapy. The intrinsic brilliance of the flame of all these arcs is relatively low, but the size of the flame is stated to give volume and efficiency.[65]

The effects of various proportions of iron in the anode on the spectrum of the carbon arc have been determined by Reiniers.[66] With 30 to 90 per cent of iron, the cyanogen band could still be detected, but most of the other bands disappeared when 2 per cent of iron was present, with the exception of those at 5152-5159A. The latter can still be detected with 25 per cent iron in the carbon.

Peczalski[67] has shown that the spectrum of the internal layers of an arc salted with calcium fluoride consists principally of calcium fluoride bands.[68] Reiter and

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[64] Greider, C. E., U. S P 1,920,255, Aug 1, 1933 (to National Carbon Co.). See, however, O'Brien, B, U. S. P 2,121,882, June 28 1938, *Chem Abs.* **32**, 6353 (1938).

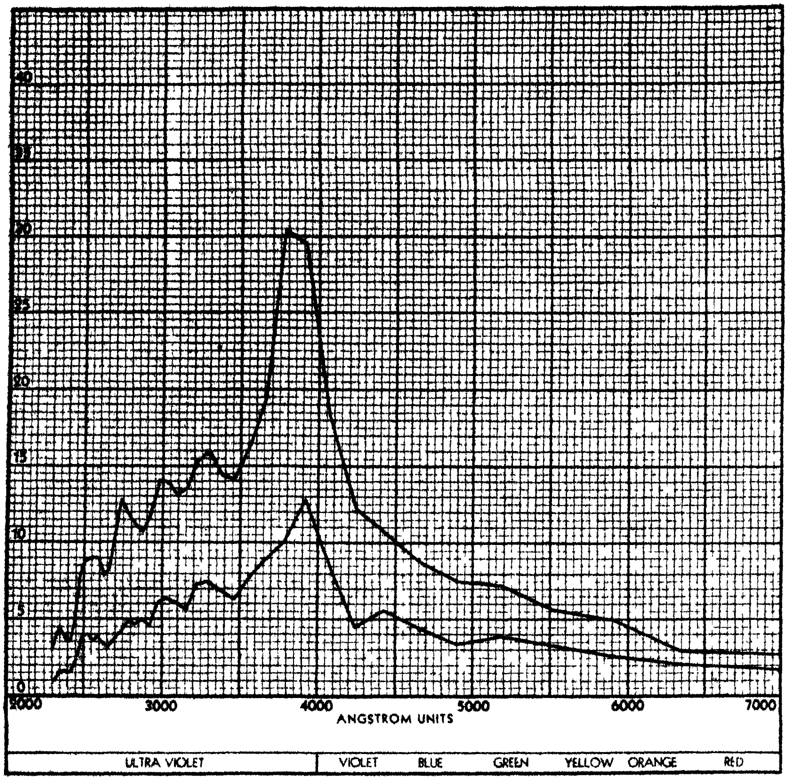
[65] Extensive studies of the emission of various carbons have also been made at the Bureau of Standards. Coblentz, W. W., Dorcas, M J, and Hughes, C. W., *Sci Papers Bureau Standards*, **21**, No. 539 (1926); Coblentz, W. W, *Am J Electrotherapeutics and Radiology*, **63**, 455 (1925).

[66] Reiniers, J. H., Jr, *Verslag Akad Wetenschappen Amsterdam*, **33**, 655 (1924); *Chem. Abs.*, **19**, 2300 (1925).

[67] Peczalski, T., *Compt rend*, **199**, 405 (1934); Szulc, N., *Ibid.*, **201**, 48 (1935).

[68] For details of the preparation of carbon electrodes containing calcium fluoride, see M. and V. Arnone, British P. 247,831, Feb 25, 1926; *Chem Abs.*, **21**, 536 (1927); and also Orne, S. W., U. S. P. 1,867,524, July 12, 1932; Canadian P. 310,628, April 21, 1931

Gabor[69] describe an arc in which at least one electrode containing silver is used in conjunction with various filters. This arc was stated to produce a strong spectrum between 3300 and 3600A, lines of wave-lengths less than 3200A being practically absent. The arc was intended for use in the stimulation of plant growth. (See, however, Chapter 44.)



(Courtesy National Carbon Co, Inc)

FIGURE 18 Spectral Energy Distribution of Therapeutic U Carbons.

For therapeutic radiations, Chesney[70] employs carbon with iron carbide and at least two ferroalloys of metals, such as uranium, tungsten, vanadium, molybdenum, yttrium, titanium, tantalum and zirconium, having complementary spectra rich in ultraviolet. E. and O. Conradty[71] add bismuth or a salt of bismuth to the core of a carbon arc.

Lavoisier[72] uses as one electrode a dehydrated and glazed mixture of zirconia and yttria. Volmer[73] uses electrodes of metal oxides, nitrides, carbides or silicates.

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[69] Reiter, T., and Gabor, D., U. S. P. 1,856,969, May 3, 1932 (to Siemens and Halske, A.-G.), *Chem. Abs.*, **26**, 3447 (1932)

[70] Chesney, J., U. S. P. 1,838,741, Dec. 29, 1931 (to U V Generator Corp.); *Chem Abs.*, **26**, 1202 (1932).

[71] Conradty, E., and Conradty, O., French P 710,913, Feb. 6, 1931; *Chem. Abs*, **26**, 1526 (1932).

[72] Lavoisier, I. J., U. S P. 1,682,847, Sept. 4, 1928 (to Burdick Corp.); *Chem Abs*, **22**, 3848 (1928).

[73] Volmer, M., British P. 418,988, Oct. 29, 1934; U. S. P. 2,074,600; *Chem Abs.*, **29**, 2454 (1931).

The metals suggested include zirconium, magnesium or aluminum with the addition of ferric oxide. Moore and Hole [74] use powdered tungsten sintered with iron and titanium and add other metals to supply radiations in any desired part of the spectrum.

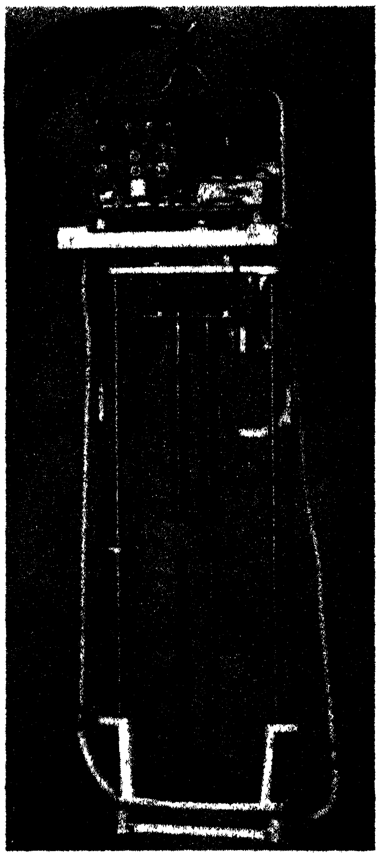

FIGURE 19.

Industrial Carbon Arc.

(Courtesy National Carbon Co., Inc.)

Unusual designs of carbon arcs have been proposed. Pauthenier [75] used a rotating arc and Pierucci [76] employed an electrolyte as one electrode of an alternating current carbon arc. Rocard and de Rothschild [77] direct gas currents along the electrodes. According to Gauthier, Le Bozec and Dubois,[78] a cathode for rotary flame arcs comprises a hollow annular ring in which a cooling liquid flows continuously. An apparatus for producing an electric arc in which a gaseous hydrocarbon is led between two concentric carbon electrodes has been described.[79]

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[74] Moore, W. G., and Hole, K. W., British P. 450,552, July 20, 1936; Moore, W. G., British P. 245,872; *Chem. Abs*, **21**, 363 (1927).

[75] Pauthenier, *Compt. rend.*, **180**, 1834 (1925).

[76] Pierucci, M., *Nuovo cimento*, **12**, 1 (1935); *Chem. Abs*, **29**, 3607 (1935).

[77] Rocard, Y. A, and de Rothschild, P., British P. 287,160, March 17, 1927.

[78] Gauthier, G., Le Bozec, L., and Dubois, R., U. S. P. 1,793,605, Feb. 24, 1931; *Chem. Abs.*, **25**, 2061 (1931).

For commercial arcs intended as photochemical sources, some type of automatic feed for one or both of the poles is necessary to keep the arc length constant though the pole materials suffer destruction. In some instances an electromagnetic device is employed which alters the distance between poles as the current through the arc changes. A method based upon thermostatic control has been advocated by Patterson.[80] Photoelectric control [81] has also been proposed.[82]

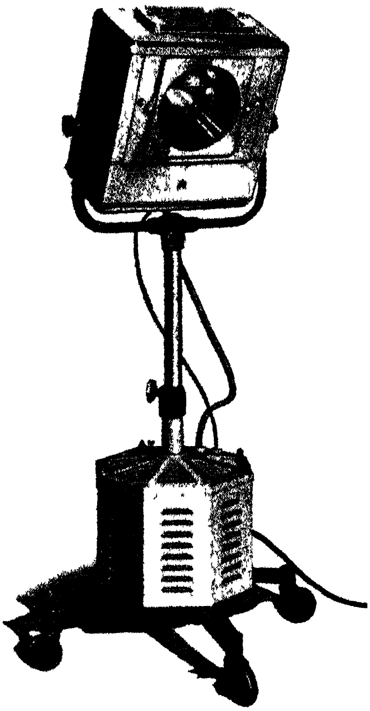

FIGURE 20.

Eveready Model A-2 Carbon Arc Lamp.

(Courtesy National Carbon Co, Inc.)

Industrial arc installations have been developed by the National Carbon Co. (Figure 19.)[83] Such arcs are reported to operate for ten hours or more without attention, and to be capable of remote or automatic control. It is claimed the ultraviolet shorter than 4000A can be produced by this arc in commercial quantities with a switchboard efficiency of over 12 per cent. A typical medium-sized unit uses 3 kilowatts (59 volts, 60 amperes) directly from a 220-volt a.c. line through transformers. With "C" carbons, it would give about 50×10^{-6} watt per square millimeter (at one meter horizontal distance from the arc) of radiation shorter than 6500A. About half of this radiation is in the ultraviolet range. Each square meter (and there are 12.5 such around the arc) can be irradiated with 25 watts of ultraviolet. Such units are of value in the food and stock- and poultry-feed industries.

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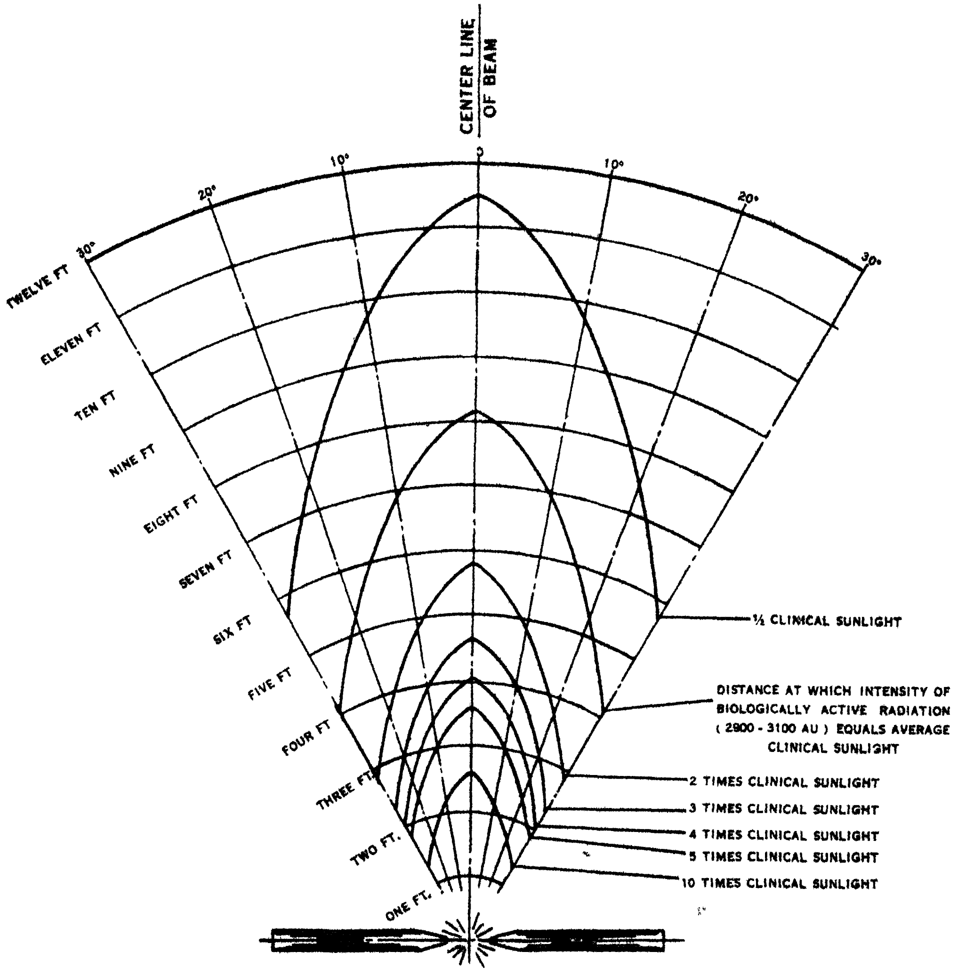
[79] Presslicht-Patent-Verwertungsgesellschaft, German P. 579,682, June 29, 1933; *Chem. Abs.*, **28**, 980 (1934).

[80] Patterson, M. L, U. S. P. 1,778,770, Oct. 21, 1931; *Chem. Abs*, **25**, 6 (1931).

[81] Lennox, E. A., British P. 383,853, Nov. 24, 1932.

[82] Other details of mechanical construction and control: Tappan, C., British P. 412,844, July 5, 1934; Boardman, R., British P. 372,552, May 1, 1931; Taylor, A., and Heathcote, R., British P. 416,170, Sept. 13, 1934; Woerner, H. B., U. S P. 1,705,798, March 19, 1929; Siemens-Schuckert Werke, British P. 390,624, April 13, 1933; Robinson, F. W., British P. 379,524 Sept. 1, 1932; Zeiss Ikon, A.-G., British P. 381,452, Oct. 6, 1932; 414,316, Aug. 2, 1934; 405,597, Feb 8, 1934; Hall, B. J., British P. 396,876, Aug. 17, 1933; Anderson, N. J., and Rigby, R., Ltd., British P. 391,059, April 20, 1933; Cricks, Rigby and Rigby, Ltd, British P. 400,692, Nov. 2, 1933; Volmer, M., U. S. P. 2,004,680, June 1, 1935; British P. 418,988, Oct. 29, 1934.

[84] Dorcas, M. J., *Ind. Eng. Chem.*, **22**, 1244 (1930).


CENTER LINE OF BEAM
30°
20°
10°
0
10°
20°
30°
TWELVE FT
ELEVEN FT
TEN FT
NINE FT
EIGHT FT
SEVEN FT
SIX FT
FIVE FT
FOUR FT
THREE FT
TWO FT.
ONE FT.
½ CLINICAL SUNLIGHT
DISTANCE AT WHICH INTENSITY OF BIOLOGICALLY ACTIVE RADIATION (2900 - 3100 AU) EQUALS AVERAGE CLINICAL SUNLIGHT
2 TIMES CLINICAL SUNLIGHT
3 TIMES CLINICAL SUNLIGHT
4 TIMES CLINICAL SUNLIGHT
5 TIMES CLINICAL SUNLIGHT
10 TIMES CLINICAL SUNLIGHT

(Courtesy National Carbon Co., Inc.)

FIGURE 21. Curves of Uniform, High-intensity Sunshine Carbons.

Arc lamps with special housings are available (Figure 20) equipped with a removable Corex D glass filter for lessening the output of radiations shorter than 2900A. The lamp uses 115-volt, 60-cycle alternating current. Figure 21 indicates the intensities of the 2900 to 3100A radiations at various positions with respect to the center of the beam, as compared with their intensities in average sunlight. A simpler form of arc lamp (Figure 22) is also utilized. These lamps may be equipped with adaptors and applicators for irradiation of small areas. (Figure 23.) Large motor-fed solarium units (one-arc, two-arc and four-arc types) make possible the treatment of from 18 to 20 patients at one time (Figure 24) and are in use in many hospitals, schools and sanatoria. Such units,[84] also adapted to clubs and swimming pools, use carbons 12 feet long. The arc burns between only one pair of carbons at a time, shifting to another set every half hour as the carbons burn back. One trim of carbons burns continuously for 12 hours if operated at 45 amperes, ten hours at 60 amperes or 8 hours at 90 amperes.

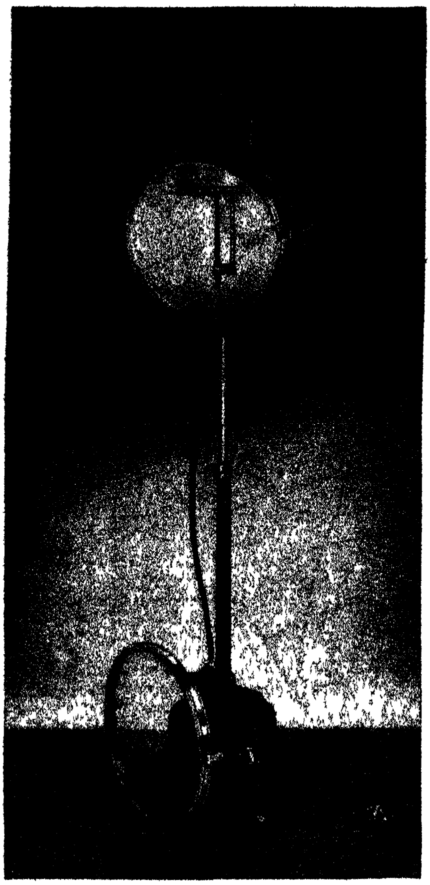


FIGURE 22.

Eveready Model L 1 Lamp

(Courtesy National Carbon Co., Inc.)

An arc for splitting hydrocarbon gases to acetylene and hydrogen and for synthesizing hydrogen cyanide has been described.[85] The zinc-graphite arc has been employed under liquids as a reducing agent.[86] Under carbon disulfide, the optimum yield of carbon subsulfide was almost 50 per cent of that represented by the reaction:

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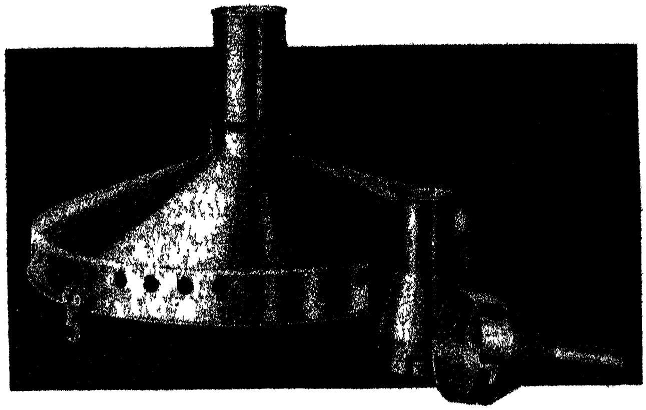
[84] Kalb, W. C., *J. Am. Inst. Elec. Eng.*, **49**, 1031 (1930).

[85] Soc. pour l'ind. chim Bâle, German P. 607,331, Dec. 21, 1934; British P. 389,761. See also Briner, E., Desbaillets, J., and Paillard, H., *Helv. Chim. Acta*, **21**, 115 (1938).

[86] Stock A. Brandt, A., and Fischer, H., *Ber.* **58B**, 643 (1925).



(Courtesy National Carbon Co, Inc)

FIGURE 23 Adaptor and Applicators for Model L-1 Lamp.

FIGURE 24 Solarium Carbon-Arc Equipment.

$3CS_2 + 4Zn \rightarrow C_3S_2 + 4ZnS$. With silicon tetrachloride, a stationary aluminum cathode and movable zinc anode, the main reaction at $-55°$ to $-15°$ consists in the production of zinc chloride and silicon, a minor portion of the silicon tetrachloride being converted into hexachlorodisilane. Under similar conditions, phosphorus trichloride yields yellow phosphorus and zinc chloride, together with small amounts of phosphorus dichloride, P_2Cl_4. Boron trichloride is converted into boron; to a minor extent a chloride, B_2Cl_4, is produced but the latter was not freed completely from silicon tetrachloride, present as impurity in the boron trichloride used.

Maslowski and Regulski [87] have produced zinc nitride, Zn_8N_2, by an arc between zinc electrodes in nitrogen at a pressure below 25 mm.

Under-water operation of an arc has been employed as a method for disintegrating the electrode materials. This is the basis of the Bredig method for the preparation of colloidal suspensions, the details of which have been summarized by Svedberg.[88] Carter and Campbell [89] have studied the gaseous products formed during the operation of the carbon arc under water. The average composition of the products was 9.8 per cent carbon dioxide, 18.1 per cent carbon monoxide, 3.3 per cent oxygen, 49.3 per cent hydrogen, 3.2 per cent saturated hydrocarbons and 14.6 per cent residual gas, mostly nitrogen. Finely dispersed graphitic acid also was formed.

Plotnikow [90] has described accessory equipment for rendering large and small carbon arcs suitable sources for the demonstration of the phenomena of ultraviolet fluorescence. With suitable filters, carbon arcs can be used as sources of infrared for clinical photography.

The carbon arc may also be employed in spectrographic analysis. The material to be tested may be placed within a hole drilled in the lower carbon electrode. Details of analysis are found in manuals of spectrographic analysis.[91] Acheson graphite electrodes, 0.6 mm. in diameter and 5 cm. long, are recommended. Special precautions must be taken in the purification of these electrodes.[92] Heat treatments usually are employed. The common impurities in the electrodes include vanadium, lithium, strontium, calcium, iron, titanium, barium, aluminum, boron, copper, magnesium, manganese and silicon.[93]

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[87] Maslowski, K., and Regulski, H., *Compt rend. soc. polonaise phys.*, **3**, 87 (1927), *Chem Abs.*, **23**, 5114 (1929).

[88] Svedberg, T., "Methoden zur Herstellung Kolloider Lösungen Anorganischer Stoffe," Dresden, Steinkopff, 1922.

[89] Carter, H. D., and Campbell, A. N., *Trans Electrochem. Soc.*, **63**, 419 (1933).

[90] Plotnikow, I., *Z. Elektrochem.*, **35**, 434 (1929). For a discussion of syntheses conducted in electric discharges, see Schenk, P. W., *Angew. Chem.*, **50**, 535 (1937).

[91] See also Nitchie, C. C., *Ind. Eng. Chem. (Anal. Ed.)*, **1**, 1 (1929); Wilhelm, H. A., *Ibid.*, **10**, 211 (1938).

[92] Heyne, G., *Angew. Chem.*, **45**, 612 (1932); Moritz, H., *Zentr. Mineral. Geol*, **1935A**, 284; Roach, F., *Nature*, **139**, 547 (1937); Russanow, A., *Z. anorg. allgem. Chem.*, **219**, 332 (1934); Webb, D. A., *Nature*, **139**, 248 (1937); Staud, A. H., and Ruehle, A. E., *Ind. Eng Chem (Anal. Ed.)*, **10**, 59 (1938); Owens, J. S., Peake, J. S., and Fowler, R. G, U. S. P. 2,117,497, May 17, 1938, *Chem. Abs.*, **32**, 4889 (1932). Dow Chemical Co., British P. 496,615, Jan. 3, 1938.

[93] Maltby, J. G., *Chem. & Ind.*, **1937**, 220; Standen, G. W., and Kovach, L., Jr., *Proc. Am Soc Testing Materials*, **35**, Pt. 2, 79 (1935); Gatterer, A., *Z. ver. deut. Ing.*, **80**, 129 (1936).

Chapter 6

Enclosed Vapor Arcs. The Quartz Mercury-vapor Arc

Enclosed gas and vapor arcs, of which the mercury-vapor arc is the most widely used, differ from the open arcs of the previous chapter in that the enveloping tube or bulb makes the pressure of the gas or vapor in the arc-conducting stream independent of that of the external atmosphere. The transparency of the envelope also limits the radiations available from such arcs. If, as is generally true, the arc vessel contains in liquid or solid form a relatively large quantity of the element, usually mercury, the vapor of which forms the conducting medium for the arc, the vapor pressure will depend upon the operating temperature of the arc. The voltage drop across the arc is dependent, as discussed in the preceding chapter, not only upon the nature of the electrodes, the cathode exerting the predominant effect, but also upon the nature of the gas or vapor, and its pressure. If the vessel contains a supply of unvaporized mercury, the pressure is the vapor pressure of the mercury at the temperature at any time, being very low when the arc is cool, and atmospheric or greater under certain conditions of operation. When the pressure is low, the arc fills the entire tube. When, after a starting period, the pressure of the mercury vapor rises, the arc becomes constricted to a narrow bright luminous stream, surrounded by dark mercury vapor This absorbs certain of the mercury lines by self-reversal and thus alters the energy distribution between the various mercury lines.

The mercury arc emits predominantly only a few intense lines, superposed upon a weak continuous spectrum, which is neglected in much photochemical work. Under certain conditions, a less-important banded spectrum may be observed. About 6 per cent of the total energy is of wave-lengths less than 2900A. Figure 25 shows a photograph of the spectrum of a quartz tube mercury arc, and Figure 26 shows the relative intensities of the prominent lines of the spectrum. The relative intensities of these lines are modified by the operating conditions.

The condition of the conducting gas does not limit the current as does the resistance of an electric lamp filament, so that a resistance must always be placed in series with a gaseous conduction discharge in order to operate it.

Since the mercury arc came to be recognized as a reliable source of light of short wave-lengths, the number of types of lamps embodying its use has increased rapidly.

The early forms of the mercury arc were direct outgrowths from the open arcs discussed in the previous chapter and had both electrodes of mercury. In time, it was found advantageous to replace the anode by some other metal. More recently, the tendency has been to avoid the use of mercury cathodes as well, and employ only mercury vapor for the conduction of the discharge. Lamps of this type will be discussed in Chapter 8.

EARLY HISTORY OF THE MERCURY ARC

Perkin[1] considers the observation that a brilliant light is emitted when mercury is vaporized in an electric arc to have been made originally by Wheatstone who, in 1835, described the characteristics of such a light before the British Association. Its illuminating power was not realized, however, until some time later, when in 1852 Jackson secured a patent for a mercury lamp. The latter consisted of carbon electrodes, the lower one of which had a recess to hold a small quantity of mercury, the idea being to provide a non-consuming electrode. Binks about a year later produced and patented a lamp having two mercury electrodes which were enclosed in a glass case. Provision was also made for condensing the vaporized metal to the liquid condition again. Way patented a lamp (in 1856) which was described in the London *Times* of August 3, 1860, with the claim that it produced a more brilliant light than had ever been seen before.

Harrison, in 1857, developed a lamp in which a carbon rod was suspended over a cup of mercury. In another form of lamp, mercury was caused to drop on a carbon rod. Difficulties were encountered in obtaining a steady arc, although Harrison endeavored to overcome these by means of an electro-mechanical device. In 1867, Siemens made a mercury lamp which had a vibrating electrode dipping into a mercury cup The light of this lamp was, however, of an intermittent nature. Siemens' idea was to employ this lamp for lighting buoys at sea, but apparently the device was never used for this purpose. The next attempt to produce a mercury lamp appears to have been made in 1875 by Prosser. It was a combined carbon and mercury lamp, the object being to overcome flickering, which was an unpleasant feature of the original arc lamps. Among the various other attempts to produce a satisfactory lamp must be mentioned that of Rapieff in 1879. This lamp contained a condensing chamber for the mercury vapor, and could be started by shaking the mercury or by an electro-mechanical arrangement.

In 1892, Arons showed that an arc could be produced by passing a direct current through mercury in an evacuated tube. The Arons lamp, which was five feet long, was started by tilting and, therefore, must have required a very large quantity of mercury. According to Axmann,[2] the later types of mercury vapor lamps are based on Arons's investigations upon low-pressure arcs. Thus, in 1892, Dowsing and Keating made a lamp in which an alternating current was passed through a Geissler tube containing mercury. They found it advisable to warm the mercury in order to vaporize it before starting the lamp.

The object of most of the early workers was the production of a lamp for visible illumination. The first lamp to attract attention in this connection was one displayed by Peter Cooper-Hewitt before the American Institute of Electrical Engineers at a meeting in April, 1901.[3] This lamp, the result of long experimenting, is said to have been installed first in the composing rooms of the New York *Evening Post* in 1903. Many practical difficulties, such as the inherent instability of the arc, changes in mercury vapor pressure with operating temperature, and distillation of the mercury from certain portions of the lamp, were encountered. Cooper-Hewitt later devised a lamp in which the mercury was cooled and condensed at about the same speed as that at which it vaporized.

The development of the lamp as an illuminating source for factories and drafting rooms lies beyond the scope of this book, except insofar as modifications have been successfully applied to the mercury arc in a quartz tube employed for ultraviolet emission. The reader interested in the development of the Cooper-Hewitt lamp, which is a long arc operating at a low mercury-vapor pressure, should consult the articles by Buttolph [4] of the Engineering Department of the General Electric Vapor Lamp Co. He points out that during the years 1902-07, the condensing chamber

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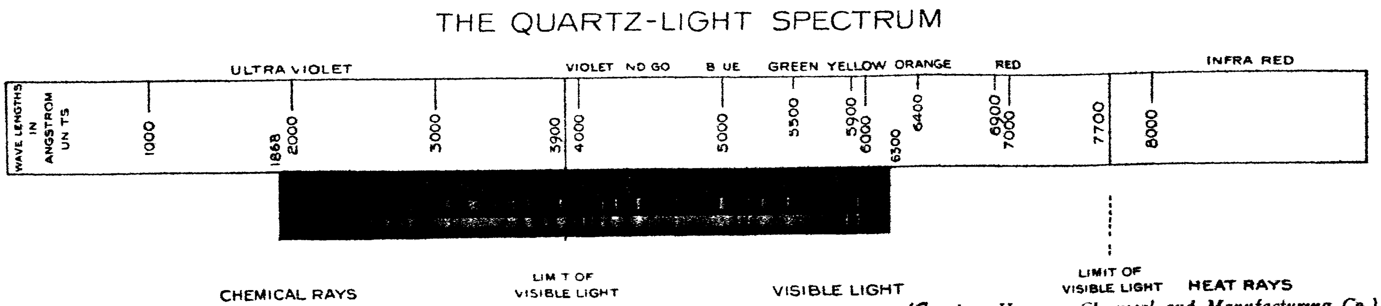
[1] Perkin, F. M, *Trans. Faraday Soc*, **6**, 199 (1911).

[2] Axmann, *Z. Phys. diatetische Ther*, **13**, 470 (1909 10)

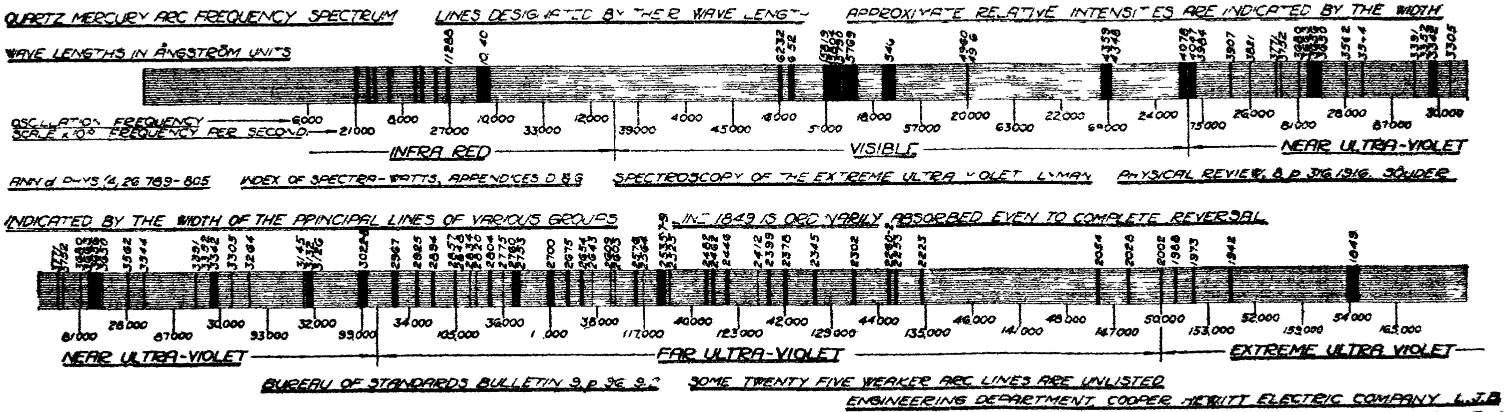
[3] Buttolph, L J, *Trans Electrochem Soc*, **65**, 143 (1934).

[4] Buttolph, L. J., *Gen Elec Rev*, **23**, 741, 858 (1920), *Rev. Sci. Instruments*, **1**, 487 (1930); *Trans. Electrochem Soc.*, **65** (1934), 143, *Trans Illum Eng Soc*, Preprint, 1932; **30**, 147 (1935). (See also, Ferguson, J B., "The Quartz Mercury Vapor Lamp" London Lewis and Co, Ltd.; and also Pierce, R F, *Illuminating Engineer*, **6**, 133 (1911).



(Courtesy Hanovia Chemical and Manufacturing Co.)

FIGURE 25 Spectrogram of Quartz-Tube Mercury Arc.


QUARTZ MERCURY ARC FREQUENCY SPECTRUM
LINES DESIGNATED BY THEIR WAVE LENGTH
APPROXIMATE RELATIVE INTENSITIES ARE INDICATED BY THE WIDTH
WAVE LENGTHS IN ÅNGSTRÖM UNITS
OSCILLATION FREQUENCY
SCALE x 10⁸ FREQUENCY PER SECOND
INFRA RED
VISIBLE
NEAR ULTRA-VIOLET
ANN d PHYS (4) 26 789-805
INDEX OF SPECTRA - WATTS, APPENDICES D & G
SPECTROSCOPY OF THE EXTREME ULTRA VIOLET LYMAN
PHYSICAL REVIEW, 8, p 316, 1916, SOUDER
INDICATED BY THE WIDTH OF THE PRINCIPAL LINES OF VARIOUS GROUPS
LINE 1849 IS ORDINARILY ABSORBED EVEN TO COMPLETE REVERSAL
NEAR ULTRA-VIOLET
FAR ULTRA-VIOLET
EXTREME ULTRA VIOLET
BUREAU OF STANDARDS BULLETIN 9, p 36 9.2
SOME TWENTY FIVE WEAKER ARC LINES ARE UNLISTED
ENGINEERING DEPARTMENT COOPER HEWITT ELECTRIC COMPANY L.J.B.

(Courtesy Hanovia Chemical and Manufacturing Co.)

FIGURE 26. Quartz Mercury Arc Frequency Spectrum.

was standardized, iron was adopted as the positive electrode material, and an automatic starting device was introduced. Between 1907 and 1910, a commercial form of alternating current lamp was developed, and in the latter year a fluorescent reflector was put on the market. During the succeeding period a so-called orthochromatic lamp and a quartz mercury lamp were developed, and the problem of operating the alternating current lamp on a high power factor was solved.

Use as a Polariscopic Source. About the earliest use adopted by the chemist for the mercury arc was as a source of light for work with the polariscope and other optical instruments.[5] At present, the tendency is to employ any usual laboratory quartz mercury arc for this purpose. Naumann [6] finds the intense light of the modern mercury lamp to increase the accuracy of such work from two to three times.

Arcs started by tilting have the disadvantage of requiring a readjustment of the slit of any fine optical apparatus after having been put into operation. To avoid this, Harries and v. Hippel [7] devised a bright, automatic starting arc which burns in any position. In a lamp possessing such an arc, a heating element produces a bubble of vapor which breaks a column of mercury in a capillary, thereby starting the arc. Such operation was based upon a lamp developed by Soltan [8] but differed in having an extension vessel which permitted the arc to be operated in any position, as well as in having an automatic starting device. The use of a narrow tube and high pressure made the usual operating current of the lamp, run at 110 volts, only 150 milliamperes.

Since lines in the visible region are commonly employed in polarimetry, a quartz arc is not necessary. A compact glass lamp of high intensity, steady operation and suitable for many optical investigations has been described by Balinkin and Wells.[9] It is a two-legged tube, the lower legs containing the mercury electrodes of unequal heights, the positive being the higher. A vertical tube above this serves as a condensing chamber. Constrictions in the lower limbs serve to retain mercury in the lower portions when the lamp is tilted for starting and so prevent the arc striking to the sealed in tungsten wires, overheating them, blackening the walls or cracking the seal. A ballast resistance is used to keep about one ampere at 35 volts across the terminals. Part of this resistance is cut out during the first half minute after the lamp has been started by tilting, so that for a brief period the newly formed arc carries three amperes.

Simple Arcs Developed in the Laboratory for Photochemical Studies. That the mercury arc might prove a valuable source for studying photochemical reactions in the ultraviolet were it enclosed in quartz soon became apparent. Such lamps were manufactured by Heraeus of Hanau in Germany as early as 1905 but, because of the expense of the quartz tubing, they remained laboratory curiosities for several years. As silica tubing became available, such lamps were used occasionally in a few laboratories. Recently, a number of workers have resumed investigations with laboratory-made quartz mercury arcs.

Among the first to employ a mercury arc as a source for effecting photochemical changes was Fischer,[10] who used it in studies on the formation of ozone. He fixed an exhausted double-walled quartz cylinder B (Figure 27) with sealing wax into the neck of a surrounding cylindrical glass vessel A, connected with an air pump by the tube F. The anode consisted of an iron ring K, surrounding the quartz cylinder and suspended by means of two platinum wires fused into the walls of the glass vessel. Mercury in the bottom of the latter served as cathode. The lamp was operated at 20 volts and 5 amperes, and was started by means of an induction coil. Arrangements were made to cool the lamp both internally and externally, so that the temperature in the interior of the lamp was kept down, thus maintaining a low density of the mercury vapor.

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[5] Disch, J., *Ann. Phys.*, **12**, 1155 (1903); Schönrock, O., *Z. Verein. Deutsch. Zuckerind.*, **53**, 652 (1903); Lowry, T. M., *Trans. Faraday Soc.*, **7**, 267 (1912).

[6] Naumann, H. N., *Biochem. Z.*, **229**, 269 (1930). The Osram high pressure mercury lamp is a satisfactory source for ultramicroscopy, according to K. Hoffmann, *Kolloid Z.*, **83**, 9 (1938).

[7] Harries, W., and v. Hippel, A., *Physik. Z.*, **33**, 81 (1932).

[8] Soltan, A., *Compt. rend. Pol. Phys.*, **4**, 301 (1929).

[9] Balinkin, I. A., and Wells, D. A., *Rev. Sci. Instruments*, **3**, 388 (1932).

[10] Fischer, F., *Ber.*, **38**, 2630 (1905).

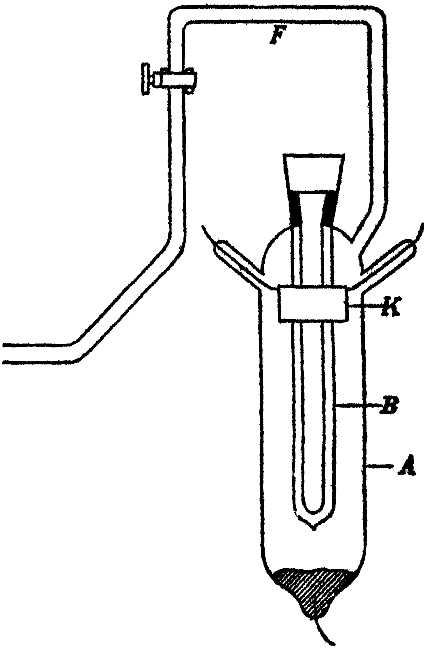

FIGURE 27.

Fisher's Lamp for Formation of Ozone.

Chapman, Chadwick and Ramsbottom[11] employed a similar principle in effecting gas reactions in a quartz bulb (Figure 28) enclosed in a glass mercury lamp in which the cathode was a pool of mercury and the anode a short cylinder of iron suspended in the upper part of the exhausted glass container. A somewhat more complex lamp, although very similar in principle, was used by Coehn and Becker[12] in their work on the oxidation of sulfur dioxide. (Figure 29.) The lamp consists of a glass vessel (4) in which the double-walled quartz vessel (2 and 3) is placed. A mercury seal is used at the top of the vessel (4). The lamp is located in the water-jacket or cooling vessel (5). To make the burning uniform a magnet (M) is placed in a glass tube in the lamp as shown. A quartz tube (1) is inserted in the vessel (2) through which gases may be passed by means of the inlet and outlet tubes (G).

Weigert[13] bent the arc tube into a U-shape, and arranged the apparatus for

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[11] Chapman, D. L., Chadwick, S., and Ramsbottom, J. E., *J. Chem. Soc.*, **91**, 945 (1907).
[12] Coehn, A., and Becker, H., *Z. physik. Chem.*, **70**, 90 (1910); *Z. Elektrochem.*, **13**, 545 (1907).
[13] Weigert, F., *Z. physik. Chem.*, **80**, 67 (1912).

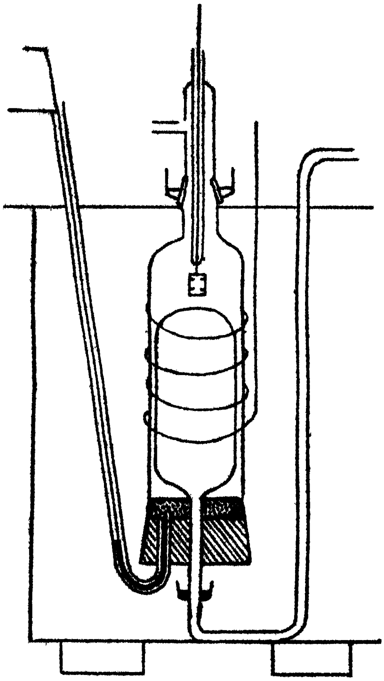

FIGURE 28.
Gas Irradiation Apparatus.

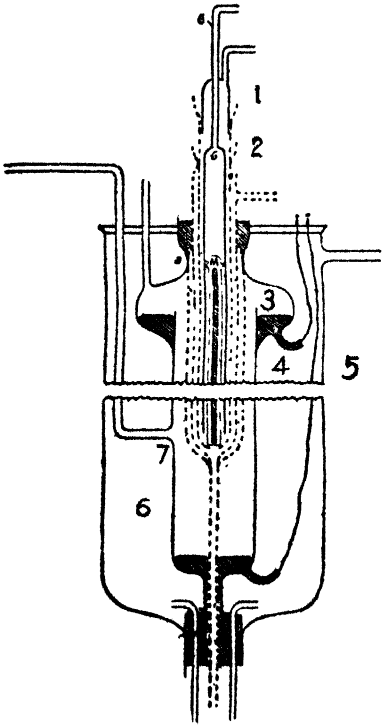

FIGURE 29.

water cooling so as to avoid the effects of heat (from the lamp) on the reactions under investigation. He surrounded the lamp by the reacting gases, the vessel containing them being in turn immersed in the cooling water. (Figure 30.) A mercury arc was formed in the inverted U-tube B between surfaces of mercury E_1 and E_2, electrical connection being made at K_1 and K_2. The apparatus was mounted in a watertight casing having a quartz plate serving as a window if external exposures were to be made also.

Bovie[14] constructed several lamps for biological experiments; these were not difficult to make and the design could be altered readily to suit particular requirements. Figure 31 shows a simple form based upon a lamp made by Kraus. A is a quartz tube one centimeter in diameter. One end is bent downward to form the positive electrode C. A quartz tube of the same diameter is sealed in, near the other end, to form the negative electrode B. The distance between B and C is about 10 cm. The end of the tube A forms a condenser. The lamp is sealed, after exhaustion of gases at H. The tube A should be inclined to the horizontal position at an angle of 6° to 7°, the end (J) being higher, so that the condensed mercury

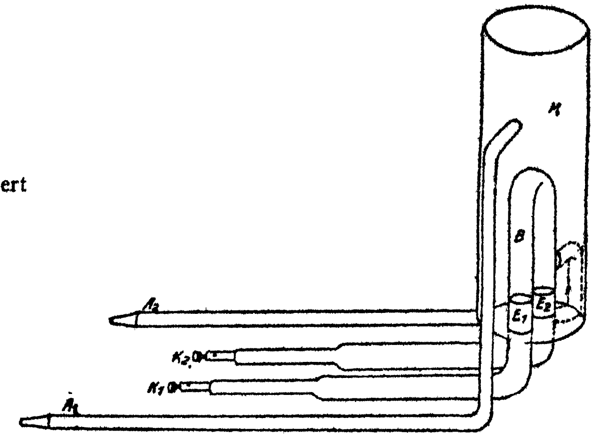

FIGURE 30.

Lamp Employed by Weigert for Treatment of Gases.

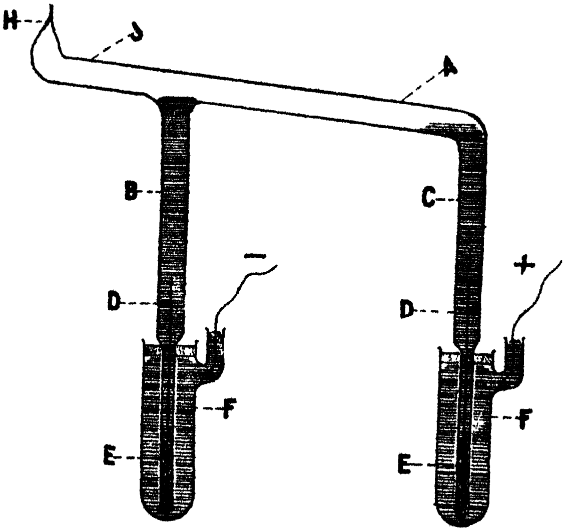

FIGURE 31.

Lamp Used by Bovie for Biological Work.

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[14] Bovie, W. T., *J. Biol. Chem.*, 20, 315 (1915).

will flow back into C. Pieces of five-millimeter quartz tubing are sealed to the lower ends of B and C. These in turn are set in mercury cisterns F,F (made of glass); test tubes may be used. The small tubes are sealed at E. The detail of the seal is shown in Figure 32. A bulb of wax on the outside is necessary in order to make the seal air-tight. The iron wire D conducts the electric current through the wax seal. The lamp should be used on a 110 volt direct-current circuit with five or six 16 c.p. bulbs in multiple as resistance, and will carry from 1.25 to 1.5 amperes, depending on the amount of cooling at the electrodes B and C.

Hulbert[15] has described a simple laboratory lamp made of Pyrex or quartz, so designed that the seals for the electrodes and for the stopcock (through which the lamp is exhausted) can be made of wax. It will run normally for twenty hours or more before it requires re-exhausting. Another easily constructed lamp is due to Allen.[16]

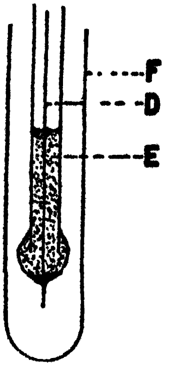

Figure 32.

Construction of Seal.

Arcs in glass with thin Pyrex windows, which were almost as efficient as quartz in transmitting ultraviolet, were described by Sonkin[17] as inexpensive substitutes for the quartz mercury arc for spectrographic purposes. An apparatus for the production of radiations useful in accelerating the synthesis of formaldehyde from carbon monoxide and hydrogen has been proposed by Spindler.[18] It involves the production of very hot arcs in mercury vapor at a pressure of several hundred kilograms, in a special steel furnace. Quartz or fluorite windows are provided.

The Development of the Commercial Quartz Mercury Arc

Fundamental investigations of the operation of the mercury arc were early conducted by Küch and Retschinsky of the Heraeus firm at Hanau in Germany, about 1905 to 1907. Shortly after this, that firm manufactured a quartz mercury arc. The Cooper-Hewitt Co. began the manufacture of quartz lamps about 1910. During the early developmental period the problems to be solved concerned chiefly the nature of the electrodes and their function, the making of satisfactory seals for the electrical leads, the mechanism for starting the arc, the instability of the arc, and the relation of the pressure of the mercury vapor to the energy distribution and intensity of the radiations emitted.

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[15] Hulburt, E. O., *J. Opt. Soc. Am.*, **12**, 519 (1926).
[16] Allen, A. J., *Science*, **83**, 336 (1936).
[17] Sonkin, S., *J. Opt. Soc. Am.*, **19**, 65 (1929).
[18] Spindler, H., U. S. P. 1,880,333, October 4, 1932.

NATURE OF THE ELECTRODES

1. Lamps With Both Electrodes of Mercury. As the early arcs were a direct outgrowth of the carbon or iron arcs, it was usually felt necessary to have both of the electrodes pools of mercury. The arc was formed by so tilting the lamp as to make a mercury contact between the two pools and then in some manner breaking the column of mercury, the newly formed arc driving the mercury back into the pools in the electrode vessels.

Such lamps required elaborate temperature control by means of metal heat-radiating fans to maintain the proper distribution of mercury between the electrodes, or else it was necessary to introduce a suitable condensing chamber for the mercury. Bachmann[19] claimed the elimination of this difficulty by using an anode of metal or alloy, the surface of which is amalgamated anew from time to time by means of mercury supplied from near the electrode.

Kent and Lacell[20] equalized the anode and cathode temperatures by bending the quartz tubes so that the electrodes were adjacent to each other. This was believed to prevent distillation of mercury from the hotter anode to the cathode, thereby extinguishing the arc. Belleaud and Barrollier[21] used a heat conductor surrounding the electrodes to equalize their temperatures. They[22] described a lamp to be immersed in a liquid to be sterilized, in which the cathode was screened from the liquid so that it was permitted to reach a temperature equilibrium with the anode. The mercury at the cathode automatically adjusted itself to a height favorable for operation depending upon the characteristics of the tube and the supply current.

There seem to be no direct early determinations to show whether the anode is, indeed, hotter than the cathode. In the lamp of Kelvin, Bottomley and Baird, it is the cathode which is cooled by aluminum radiating fans.

Von Recklinghausen[23] described elaborate methods for ensuring the proper distribution of mercury in lamps having a series of electrodes, now seldom employed.

To avoid the danger of breakage by mercury "slaps" during transportation of the lamp, von Türkenburg[24] filled the entire burner with mercury. During operation, mercury is displaced by the arc into a deformable anode receiver of rubber, provided with adequate cooling arrangements.

2. Lamps with Anodes of Other Materials. It soon became apparent that these difficulties might be avoided by using other materials for the anode. An iron anode was proposed by Fischer for the lamp previously described. Tian[25] made a lamp of a tube of transparent quartz through the center of which an insulated iron wire passed making contact with a drop of mercury (the cathode) at the bottom. The anode was a small iron cylinder. Ordinarily, direct current was used, but alternating current could be used if the anode was made double, *i.e.*, of two plates separated by a sheet of mica. This form of lamp had the advantage, besides low voltage operation, of being of a shape convenient for immersion in liquids. An early Cooper-Hewitt lamp[26] also employed iron as the positive electrode. Asada[27] used a brine-cooled steel anode which extended into the interior of the lamp and kept the temperature from getting too high, even when the lamp carried 20 amperes.

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[19] Bachmann, P., German P. 336,570, May 11, 1920; *J. Soc. Chem. Ind.*, **40**, 575A (1921).

[20] Kent, H. A., and Lacell, H. G., British P. 21,834 (1908).

[21] Belleand, R. L. M, and Barrollier, J., British P. 168,022, Dec. 10, 1920; 211,455, Jan. 25, 1924.

[22] Belleaud, R. L. M., and Barrollier, J., U. S. P. 1,656,898, Jan. 24, 1928.

[23] von Recklinghausen, M., U. S. P. 1,091,244, March 24, 1914, and 1,110,574, Sept. 15, 1914.

[24] von Türkenburg, F. R., U. S. P. 1,896,651, Feb. 7, 1933.

[25] Tian, A., *Compt. rend.*, **156**, 1063 (1913).

Carbon was employed for this purpose by Axmann[28] and by Kerschbaum,[29] the latter using nickel-steel pins to bring in the current. Perkin[30] mentioned the use of a tantalum button, in conjunction with mercury, for starting.

Because of its high melting point, tungsten was employed as anode by Urbain, Scal and Feige.[31] It was then necessary to avoid even the smallest trace of oxygen or the walls of the enclosing vessel became darkened because of the production of volatile oxides. The use of tungsten was adopted in the lamps of George[32] and of Nutting.[33]

Sealed-in Leads. In order to produce vacuum-tight joints between the leading-in wires and quartz, Heraeus[34] proposed to use wires of iron or other metal having a temperature coefficient of expansion considerably greater than that of quartz. The diameter of the wire was to be such that the joint remained vacuum-tight at the highest anticipated temperature, the joint being reinforced by cements which melt at such a temperature. It was stated that an iron wire of 0.5 mm. diameter affords a vacuum-tight joint in quartz-glass at a dull red heat, and wires of 0.9 mm. diameter may be heated to 360°C. without the joint leaking.

Data on the expansion of fused quartz for temperatures up to 1000°C. were given by Holborn and Henning[35] who found that the mean increase of unit length for a rise of 1° is 0.00000054. Anderson[36] pointed out that Invar (an alloy with nearly the same coefficient of expansion as quartz) leads are unsatisfactory, since Invar melts below the fusing and working temperatures of quartz. Of other available metals, tungsten and molybdenum (coefficient of expansion 4.2×10^{-6}) are nearest to the thermal expansion of quartz, but molybdenum seals are only practicable in the case of very fine wires capable of carrying no more than one ampere. It was found that the tungsten seals which had been recommended by George could not be used. Lead or mercury seals had been described by the Thermal Syndicate. Anderson developed a method of working the quartz shell onto a core of a metal (tungsten, molybdenum, tantalum, platinum) of thermal expansion less than 9.0×10^{-6} and melting point higher than that of fused quartz (1750°C.), in which heat was applied to one end while the other was evacuated. The joint was tight at only one end; the slight space at the other was filled with a mixture of hydrocarbons. These must adhere[37] to both surfaces and not absorb water or gas, must have a low vapor pressure and change slowly in viscosity with temperature. A mixture of coal-tar pitch and residues of petroleum distillates, having a viscosity at 100°C. of 2000 dyne-seconds per square centimeter, was suggested.[38]

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[26] *Elektrotechnische Z.*, **26**, 941 (1905).

[27] Asada, T., *Proc. Phys.-Math. Soc. Japan (3)* **12**, 167 (1930); *Chem. Abs.*, **25**, 254 (1931).

[28] Axmann, *Elektrotechnische Z.*, **26**, 627, 1182 (1905).

[29] Kerschbaum, F., U. S. P. 1,118,868, Nov. 24, 1914.

[30] Perkin, F. M., *Trans. Faraday Soc.*, **6**, 199 (1911).

[31] Urbain, E., Scal, C., and Feige, A., *Compt. rend.*, **152**, 255 (1911).

[32] George, H., U. S. P. 1,398,545, Nov. 29, 1921; *J. S. C. I.*, **41**, 49A (1922).

[33] Nutting, P. G., U. S. P. 1,320,087, Oct. 28, 1919, to Westinghouse Electric and Manufacturing Co.; *J. S. C. I.*, **39**, 8A (1920).

[34] Heraeus, German P. 336,014, Sept. 24, 1918; *J. Soc. Chem. Ind.*, **40**, 574A (1921).

[35] Holborn, L., and Henning, F., *Ann. Physik*, **10**, 446 (1903).

[36] Anderson, W. T., U. S. P. 1,909,797, May 16, 1933 (to Hanovia Co.).

[37] Anderson, W. T, U. S. P. 1,986,784, Jan. 8, 1935.

[38] See also British P. 356,056, Sept. 3, 1931, to Hanovia Co. for detailed discussion of a sealing arrangement. The use of rhodium coatings for the material to be sealed into quartz has recently been proposed by Harris, N. L., and Ryde, J. W., U. S. P. 2,113,984, April 12, 1938; British P. 477,462, Dec. 30, 1937; *Chem. Abs.*, **32**, 4299 (1938).

Lamps of the tungsten anode type may also be made by sealing the tungsten into glass, *e.g.*, Nonex glass (coefficient of expansion, 3.9×10^{-6}), which is then united to the quartz tube by a graded seal, employing Pyrex (3.2×10^{-6}).[39] Keyes and Kraus[40] described new glasses available for making graded seals for this purpose. They contained various proportions of titanium and vanadium oxides, as well as boron oxide. Successive rings cut from tubes of these glasses were fused onto the silica tube. In the earlier lamps employing complicated seals, overheating of the seals had to be avoided by the use of metal radiating fins. A general discussion of such joints has been given by Buttolph.[41] An ingenious method of sealing the annular ring guards at the anode and cathode of the silica tube so that they will be snug at the operating temperature of 400° C., and still not crush the silica tube on cooling, has been described by him in a patent which must be consulted for details.[42]

Methods of Starting the Discharge. Most quartz mercury arcs with either both electrodes or cathode only of mercury are started by tilting the lamp to form electrical contact by liquid mercury between the electrodes. Then, on again tilting the lamp back to its former position, the contact is broken and the arc is formed. Such a method was adopted in a water-cooled lamp of the Heraeus type used by Foster in 1906.[43]

Parisi[44] describes a mercury arc enclosed in a two-by-five-inch quartz bulb, equipped with an Edison socket, for operation on an ordinary direct-current lighting circuit. The lead-in wires, equipped with special mercury seals, are connected through wire resistance coils separated by quartz slabs, to two half-inch pools of mercury in separate enlargements at the base of the lamp bulb. The lamp is started by tilting. The coils then become incandescent, heat the mercury vapor, or retard its condensation, and thereby add to the intensity of the ultraviolet emitted.

The design of certain proposed forms of the mercury arc lamp precluded the ordinary method of starting by tilting, and a number of ingenious, but relatively seldom employed, starting devices have been suggested. An electromagnet served to bring an iron anode into contact with the mercury cathode in one type of lamp developed by the General Electric Co. as well as in that devised by Hulburt.[45] In the lamp of Gallois,[46] mercury in the initial position fills the quartz illuminating tube. When the current is applied, a coil attracts an armature connected by a rod with the tube, and turns the latter on its axis about 40°, whereby, in consequence of the shape of the tube, the mercury is divided into two portions and an arc is formed across the intervening space.

At one time, Buttolph[47] proposed to seal the arc tube to the leads by the mercury itself, the ends of the arc tube being extended into mercury-filled boxes. By means of pistons, the mercury could then be forced into the tube to form a contact and start the arc.[48]

Ulbrich[49] uses a wall to partly separate the anode mercury from the tube space;

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[39] See also Goltstein, E., British Patent Application (void), 290,632.

[40] Keyes, F. G., and Kraus, C. A., U. S. P. 1,014,757.

[41] Buttolph, L. J., *J. Opt. Soc. Am*, **11**, 549 (1925).

[42] Buttolph, L. J., British P. 376,686, July 14, 1932.

[43] Foster, G. W. A., *J. Chem. Soc.*, **89**, 913 (1906).

[44] Parisi, M., U. S. P. 1,954,888, April 17, 1934; 1,960,503, May 29, 1934 (to Goldberg, I.).

[45] Hulburt, E. O., U. S. P. 1,907,386, May 2, 1933.

[46] Gallois, J., *Bull. soc. encour, ind. nat. 121.*

[47] Buttolph, L. J., U. S. P. 1,831,998, Nov. 17, 1931.

[48] For special means of facilitating the starting of alternating current arcs, see Asada, T., *J. Inst. Elect. Eng., (Japan)*, **51**, 51 (1931); Steinmann, A., British P. 356,355, Sept. 10, 1931; Matouch, R., U. S. P. 1,750,482; Sperti, G., U. S. P. 1,889,079, Nov. 29, 1932.

[49] Ulbrich, W., U. S. P. 1,694,836, Dec. 11, 1928.

from the wall, one or more fine tubes extend the length of the tube, but are located outside of the luminous band. On tilting the lamp, mercury passes through the fine openings, so that it reaches the cathode from the end of the tube in a fine stream or streams. The use of the latter in starting avoids a sudden onrush of mercury, which might extinguish the newly formed arc, on restoring the arc to its normal position.

The lamp of Kent and Lacell[50] was started by electrically heating a small coil of wire placed around the arc tube. When started, the current was automatically cut off from the heating wire. This lamp, which was not evacuated, was burned on a 500 to 1000 volt circuit, and was extremely powerful. Preheating coils, which vaporize some of the mercury in about a minute to form contact with the anode and start the arc, have been used in various lamps. Their use also shortens the build-up period during which a steady ultraviolet intensity becomes established. A number of patents describe such devices.[51]

Electrical Starting Devices. For large-scale installations, for arcs of peculiar design to meet special irradiation conditions, and particularly for the long, low-pressure Cooper-Hewitt illuminating apparatus, the arc is usually formed by special auxiliary electrical equipment. In each instance there are involved, according to Buttolph,[52] who has reviewed the subject in detail, both the formation and maintenance of a hot spot on the cathode surface and the coincident ionization of mercury vapor between the electrodes.

With some types of arcs, the initial resistance was overcome by the aid of an induction coil, but this is usually impractical for large industrial arcs. In certain cases, however, in which the cathode spot has been formed and maintained by a small local arc to an auxiliary anode, or in which independently heated Wehnelt cathodes (see Chapter 8) are used, ionization of the vapor through the arc tube may be brought about by small Ruhmkorff coils of the kind commonly used as leak testers in high vacuum work with glass apparatus.

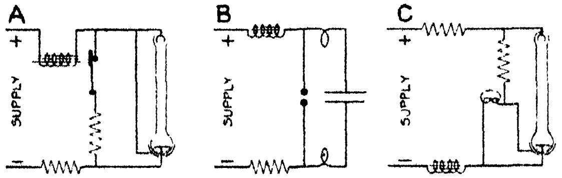

FIGURE 33. Circuits for Starting Mercury Arcs (Buttolph and Dana, *Review Scientific Instruments*).

Buttolph and Dana[53] state that the use of the operating reactance as a source of induced high voltage for arc starting (Figure 33, A) was described in patents applied for by Peter Cooper-Hewitt in 1900 to 1902. At this time the "inductance coil" was generally placed in the circuit adjacent to the arc anode, with an electrolytic interrupter or magnetically operated coil switch in multiple with the arc tube. Resistance in series with the interrupter switch kept the current sufficiently low so that it could be handled by the switch. The inductance of the lead wires, the capacity of the arc tube and the switch arc as indicated in the functional diagram B, constitute an elementary oscillatory circuit receiving its energy from the inductance coil. Such a circuit has a very high frequency and low efficiency. The effectiveness of the circuit depends upon the effectiveness of the interrupter switch, called a shifter. A high capacity mercury interrupter,[54] originally devised by Hewitt to take the place of the generally used spark-gaps in high-frequency generators, was adapted by Thomas [55] for use as a shifter switch in a starting circuit schematically shown in diagram C. When the apparatus is connected with the supply line, current flows through the auxiliary circuit, and the magnetic field of the inductance rotates the shifter switch forming a transient unstable arc in it. The resistance in series with the shifter is of an amount which makes the current too small to maintain the cathode hot spot. Furthermore, the stability of the shifter arc is decreased by the condenser between the mercury in the main arc and a tin-foil coating on the outside of the mercury chamber. When, after about 0.05 second, the arc is extinguished, the energy of the inductance is delivered as a single steep polarized wave-front impulse which tends to induce a negative potential of several thousand volts on the mercury cathode of the main arc. From an irregularity in the surface of the mercury formed by a coating of carborundum crystals fused into the glass, a localized discharge passes into the gas space and starts the main arc.[56]

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[50] Kent, H. A., and Lacell, H. G., British P. 21,834 (1908); Perkin, F. M., *Trans. Faraday Soc.*, 6, 199 (1911).

[51] Thompson, A., U. S. P. 1,962,106, June 5, 1934; Hulett, M., U. S. P. 1,886,400, Nov. 8, 1932; Blake, G. J., and Leadbetter, G., British P. 294,288, July 23, 1928.

[52] Buttolph, L. J., *Rev. Sci. Instruments*, 1, 498 (1930).

[53] Buttolph, L. J., and Dana, D. W., *Rev. Sci. Instruments*, 4, 206 (1933).

Inert gases are also used in starting arcs. At first they were employed to strike the arc by breaking the mercury column when pumped into the lamp by some suitable arrangement.

In general, however, they serve as conductors through the discharge space until enough mercury has been vaporized to carry the arc. Bayle, Fabre and George [57] found that a direct-current, quartz mercury lamp containing argon at a pressure of 500 mm. of mercury, strikes instantaneously on application of the voltage and relights automatically if the arc should happen to be extinguished. Geffcken and Richter [58] believed argon the most suitable noble gas to use for this purpose. (See also Chapter 8.)

The Pressure of the Mercury Vapor. Various methods for improving the vacuum [59] or for exhausting the lamp space have been described.[60] During the earlier development of the Cooper-Hewitt and other commercial arcs, it was generally believed that to produce a stable arc, a low pressure of mercury vapor is essential. Kent and Lacell,[61] however, recognized that increased pressure is not the cause of the instability of the arc. Evidence in favor of the use of a higher mercury vapor pressure was afforded by Henri [62] in experiments which demonstrated that the ultraviolet radiation from a mercury vapor lamp becomes more intense as the temperature of the luminous tube is allowed to rise. By cooling the tube with water, the radiation was found to be fourteen times less powerful than with air-cooling, the same number of watts being consumed. A number of lamps were introduced in which the mercury vapor pressure was atmospheric or greater. These included the Cornu type lamps, the Kelvin, Bottomley and Baird lamp and others.[63] Bernhardt[64] built a mercury lamp which burned in carbon dioxide of up to 650 atmospheres pressure and carrying 400 amperes.

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[54] Pierce, G. W., *Proc. Am. Acad. Sci.*, **39**, 389 (1904).

[55] Thomas, P. H., U. S. P. 1,079,380 (1906).

[56] For details of means for securing mercury surfaces effective for starting, see patents of Winninghoff, W. J., U. S. P. 1,831,985-6 (1931) and 1,971,945, Aug. 28, 1934; British P. 288,737, April 19, 1928. Another description of an electrical starting mechanism is given by the Schering-Kahlbaum, A.-G., British P. 364,356 and 364,393.

[57] Bayle, E., Fabre, R., and George, H., *Bull. Soc. Chim.*, **37**, 89 (1925); *Rev. d'optique*, 1 (1925).

[58] Geffcken, H., and Richter, H., British Patent Application (void), 267,127. See for a limitation of the proportion of rare gas, N. V. Phillips' Gloeilampenfabrieken, British P. 474,192, Oct. 27, 1937; *Chem. Abs.*, **32**, 2854 (1938).

[59] von Recklinghausen, M., U. S. P. 1,110,576, Sept. 15, 1914; Thompson, W. P., British P. 28,757, Dec. 20, 1911; *Chem. Abs.*, **7**, 1846 (1913); Helbronner, A., and von Recklinghausen, M., British P. 14,129, June 10, 1910.

[60] Bovie, W. T., *J. Am. Chem. Soc.*, **37**, 1721 (1915); Waran, H. P., *J. Sci. Instruments*, **1**, 54 (1923).

[61] Kent, H., and Lacell, H., British P. 21,834 (1908).

[62] Henri, V., *Compt. rend.*, **153**, 426 (1911).

The U-shaped lamps of which mention has been made probably owed their greater relative output of ultraviolet rays to a higher vapor pressure of mercury due to a lessening of the cooling of the adjacent mercury electrodes rather than, as had been thought, to an altered distribution of mercury. The bent tubes of such lamps, however, tended to deteriorate or become opaque since the arc in making the bend does not follow the shape of the tube. Instead, as indicated by the dotted line of Figure 34, it tended to approach the side of the curved portion of the tube nearest the center of curvature, subjecting it to an extremely high temperature. To counteract such destructive action, this portion of the tube was made of increased thickness or projections (Figure 35) were added to divert the arc stream.[65] Von Recklinghausen[66] also described methods of prolonging the life of his lamps by lining the portion near the hot cathode spot with a highly refractory material such as "titanium zircon quartz."

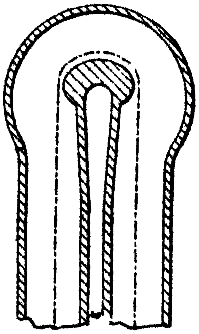

FIGURE 34.

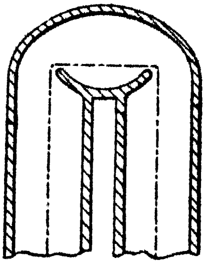

FIGURE 35

COMMERCIAL MERCURY-VAPOR ARCS (MERCURY CATHODE TYPE)

Modern commercial mercury-vapor lamps with mercury cathodes are of two main types, those having a mercury anode and those having an anode of tungsten or other metal. The first is built along the lines of the Heraeus lamp. The Hanovia quartz mercury[67] arc lamp, Figure 36, consists essentially of three parts, the tube through which the arc plays, the anode vessel and the cathode vessel. The current is carried to the lamp through nickel rods ground into the side tubes of the electrode vessels. The ground-in joints are sealed with mercury. Small quartz tubes are used in the electrode vessels to avoid "hammering" of the mercury. The lighting of the lamp is effected by turning the lever slowly around from position to position so that a stream of mercury flows from anode to cathode, making a short circuit between the two poles. On breaking the stream, the arc is struck, and the level must be brought to its original position to allow the mercury to flow back into the anode vessel. After lighting, the lamp may be turned again by the lever into a vertical position in which it can be continuously used. The arc may be used end-on in a horizontal position by viewing it from the anode end, or in a vertical position from above. On 220-volt lines the lamp may be burned at all potentials between the electrodes from 25-185 volts by means of a variable resistance of 55 to 95 ohms (depending on the type of lamp) connected in series; on 110-volt lines at all potentials from 25-80 volts by means of a variable resistance of 25 or 40 ohms. If the lamp is not required to burn at low voltages, resistances of 30 or 50 ohms and of 12 or 20 ohms suffice. At low potentials the arc or electric discharge fills the whole cross-section of the tube. With increasing potential, the cross-section of the arc diminishes more and more, and forms eventually a thread of some five millimeters diameter. The specific intensity of the visible and ultraviolet radiation is the same, and the economy equally as good in 110-volt as in 220-volt lamps. With constant external conditions the light exhibits a desirable degree of constancy. The Hanovia vapor lamp is also made for operation on alternating current, the difference in construction being that for this current it is necessary that there be two positive electrodes in place of the one ordinarily used for direct current.

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[63] U. S. P. 1,343,037; British P. 129,022 and 129,702; *J. Soc. Chem. Ind.*, 622A (1919); Beilemont, G., *Bull. soc. encour. ind. nat.*, **133**, 254 (1921); *Chem. Abs.*, **15**, 2163 (1921); Stammreich, H., *Naturwiss.*, **12**, 744 (1926).

[64] Bernhardt, F., *Physik. Z.*, **27**, 713 (1926).

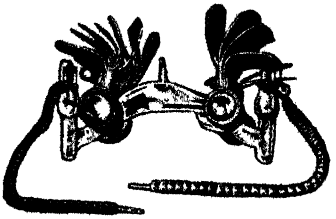
[65] von Recklinghausen, M., Helbronner, A., and Henri, V., U. S. P. 1,176,481, Aug. 29, 1916; 1,271,246, July 2, 1918.

[66] von Recklinghausen, M., U. S. P. 1,188,587, June 27, 1916.

[67] Hanovia Chemical and Manufacturing Co. (A more recent type is discussed in Chapter 8.)

FIGURE 36.

Hanovia Lamp for Direct Current.



Courtesy Hanovia Chemical and Manufacturing Co.)

Problems concerned with the design of pole vessels and the use of constrictions between these and the luminous tube to prevent alterations in the distribution of mercury during operation, have been studied by the Hanau firm.[68] By the use of a capillary at the anode, it is claimed that both vessels may be made of the same size and shape, and both may be completely filled with mercury. With alternating currents, two anode vessels have condensing chambers and separate connections by tubes with the luminous portion are necessary.

Anderson and Fraser[69] stated that in such lamps the proper temperature is usually maintained by radiation from metallic fins. If the lamp became too hot and the vapor pressure too high, the current would drop to values insufficient to maintain the cathode hot spot (which they believed to have a temperature of 2270°C.) and the arc would be extinguished. To avoid the necessity of using large volumes of mercury they proposed to immerse non-amalgamating metals of higher thermal conductivity such as wires, rods, meshes, tubes or plates of tungsten or molybdenum in the mercury in contact with the walls. Anderson [70] described methods of reducing the size of the container to one-half or one-third its previous size.

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[68] British P. 286,317, May 9, 1929.

[69] Anderson, W. T., Jr., and Fraser, H. D., U. S. P. 1,890,926, Dec. 13, 1932, to Hanovia Co.

Water-cooled lamps are usually U-shaped, as in the case of those developed by Kent and Lacell. Bird [71] designed a burner in which the effects of expansion of liquid mercury upon the positions of the two mercury levels were minimized. By dividing the anode pool by inserting a smaller tube within the anode tube, it was possible to lessen the effect of the temperature of the pool upon the vapor pressure of the arc. The small inner portion at a high temperature served as the terminal for the arc stream and the other, at a reduced temperature, acted as a receiver for the vaporized mercury. The cathode pool was believed to exert a smaller influence upon the vapor pressure than the anode pool. The area of the cathode pool was made great by means of a bulb in order to lengthen the thermal path from the arc stream to the wall.

The "hot anode" type of quartz mercury vapor lamp, known as the "Uviarc," has no mercury chamber at the anode end.[72] In place of mercury, a tungsten target composed of a spiral formed of tungsten wire is used. The anode end is protected from mechanical injury by means of a metal cap which also serves to lead the current to the anode. The cathode end is reinforced with thick quartz to absorb the shock of the mercury vapor and is set at an angle which is claimed to reflect back into the luminous portion of the tube some ultraviolet rays which would otherwise escape. The cathode end is also protected by a metal cap through which the current is led to the mercury. The tungsten wire, serving to lead the current into the lamp, is sealed into the quartz tube by a graduated mixture of quartz and glass so that at the end there is practically pure glass, while the portion next to the quartz tube is practically pure quartz. It is claimed that this combination of glass and quartz provides a proper coefficient of expansion so that the loss of vacuum is prevented. Having only one mercury electrode, this lamp is capable of being operated in either a vertical or horizontal position, which in certain cases is of advantage. A slightly different design is employed when tungsten anode ("Uviarc") lamps are intended to be run generally in a vertical or nearly vertical position. The change is principally in the construction of the cathode chamber. The Uviarc is a direct current device. It may itself function as a rectifier.[73] An alternating current Uviarc with double anode is made for certain applications.

The development of Cooper-Hewitt lamps has followed two distinct courses for visible and for ultraviolet output. The original mercury arc has been developed as a long low pressure arc for illumination of industrial establishments. LeBlanc [74] gave an early account of the construction, current consumption and efficiency of such lamps. Details of the more recent developments are to be found in the various articles of L. J. Buttolph cited in this chapter.

Our present concern is not, however, with the low-pressure illuminating arc, but rather with the high-pressure quartz arc just described. A small high intensity arc ("Labarc"), operating on 110 volts, either alternating or direct current, was described by Buttolph [75] in 1922. In it the effective light zone was one-quarter by one and three-quarter inches. It was especially suited for employment with filters, as a monochromatic light source. It was then shown that by introducing suitable resistance in series with the lamp it would function as a low-pressure arc giving only the strongest spectral lines. A detailed discussion of the operating conditions of the Uviarc is given in a following section.

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[70] Anderson, W. T., Jr, U. S. P. 1,902,936, March 28, 1933, to Hanovia Co.

[71] Bird, L. F., U. S. P. 1,952,306, March 27, 1934, to Hanovia Co.

[72] Cooper-Hewitt Electric Co., now General Electric Vapor Lamp Co.

[73] Buttolph, L. J., *Gen. Electric Rev.*, **13**, 741 (1920).

[74] LeBlanc, M., *Electrical Rev. and Western Electrician*, **57**, 1248 (1910).

[75] Buttolph, L. J., *J. Opt. Soc. Am.*, **6**, 1066 (1922).

A number of recent patents have been concerned with lamps, developed for specific purposes and with accessories as cabinets, etc. Burners enclosed in hoods may be prevented from overheating by sucking the hot air away by an electric fan attached to the upper part of the hood. According to Cooper,[76] this results in a saving of power. A cabinet for an arc for home use in therapy has been described by Link,[77] and a prepayment "coin-in-the-slot" time-switch control has been devised[78] for installations of the mercury arc in bath houses, therapeutic institutes and beauty parlors.

Therapy lamps adapted for introduction into various body cavities have been described by Philip.[79] They embody small U-tubes carrying the mercury arc, surrounded by a long, narrow quartz envelope with cooling water or gas. A number of other therapy arcs, not, however, adapted for introduction into orifices, designed by Nisbet[80] involved modifications of structural detail and new combinations of previously described principles.

To avoid the deposition of mercury on the luminescent part of a lamp intended to be submerged in water during use, Gourdon[81] located it in an evacuated vessel, the nipple of the luminescent part of the lamp passing through the wall of the vessel near the nipple of the vessel itself. This lamp was intended to be put to such curious uses as catching fish, maturing oysters and illuminating submarine operations.

An assembly of base, pedestal, hood with lips, and applicators suitable for ultraviolet therapy, has been patented by Chesney and MacLagan.[82] The Hanau firm[83] described a handle by which a therapy lamp could be carried about without danger of altering the distribution of the mercury.

The Theory of the Operation of the Mercury Arc

A. **Electrical Conduction Processes.** The general theory of the processes occurring in the arc has been treated in the previous chapter; this section deals with those processes which are especially characteristic of the arc in which the predominant conduction is by a mercury cathode and by mercury vapor in the space between the electrodes. Comparatively few investigations have been devoted to the nature of the manner in which the anode functions even in the case of the lamps of the Hanovia type in which the anode is mercury. As noted elsewhere, Compton [84] has stated that the entire problem is concentrated at the cathode, as other processes, especially those in the plasma, have been essentially explained by the work of Langmuir and Mott-Smith,[85] Tonks and Langmuir,[86] Eckart and Compton, [87] and Killian.[88]

1. *The Conduction of Current from the Cathode.* It was at first believed that the current was carried by electrons thermionically emitted from the cathode,[89] the temperature of which was then assumed to be about 2500°K. This had to be rejected when subsequent work showed that the cathode could not be hotter than

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[76] Cooper, C. A., British P. 305,758, February 14, 1929.

[77] Link, D. C., U. S. P. 1,668,566, May 8, 1928.

[78] Bar, N., v. Recsey, N., and v. Recsey, E., British P 382,349, October 27, 1932.

[79] Philip, G., British Patent Application (void), 298,903, October 15, 1928

[80] Nisbet, J., British P. 248,796, March 11, 1926.

[81] Gourdon, G., British P. 390,108, March 30, 1933.

[82] Chesney, J., and MacLagan, H. P., U. S. P. 1,813,383, July 7, 1931, to McIntosh Electrical Corp.

[83] British P. 286,318, June 4, 1929.

[84] Compton, K. T., *Phys. Rev.*, **37**, 1077 (1931).

[85] Langmuir, I., and Mott-Smith, H., *Gen. Electric Rev.*, **27**, 449,538, 616, 762, 810 (1924).

[86] Tonks, L., and Langmuir, I., *Phys. Rev*, **34**, 876 (1929).

[87] Eckart, C. H., and Compton, K. T, *Phys. Rev.*, **24**, 97 (1924).

[88] Killian, T. J., *Phys. Rev.*, **35**, 1238 (1930).

[89] Stark, J., *Ann. Physik*, **12**, 673 (1903).

600°-800°.[90] Later calculations by Compton[91] indicate the surface temperature of the cathode spot not to exceed 200°C.

Earlier observers, as Güntherschulze,[92] gave large values for the rate of vaporization of mercury from the cathode, *e.g.*, 7.2×10^{-8} gram per ampere per second. The suggestion of Compton and van Voorhis that this was in part due to mechanical loss as spray was verified by von Issendorff, who found a corrected rate of less than $0.3\text{-}1.3 \times 10^{-8}$ gram per ampere per second. Kobel[93] placed it at only 0.017×10^{-8} and Nikiforov[94] places it at only 0.4 milligram per ampere per second. This indicates but a minute loss at the cathode. These new data show that the vapor pressures at the cathode spot must be considerably less than the atmosphere or more assumed in the earlier literature.

Slepian[95] suggested that the current might be carried by positive ions arising from thermal ionization of the vapor just outside the cathode; Compton, however, objected that this theory failed to suggest a mechanism for the input of energy into the assumed high temperature region. The currently accepted theory is that of Langmuir[96] of "field currents" due to a strong field concentrated at the cathode region. The minimum value of the field was calculated by Lamar and Compton[97] to be at least 7.6×10^4 volts per centimeter. Mackeown, assuming 5 per cent of the current to be carried by positive ions, calculates it to be 5×10^5 volts per centimeter. If 1.3×10^6 volts per centimeter be assumed necessary to give the observed cathode current density of 4000 amperes per square centimeter,[98] the cathode drop will occur within a distance of 10^{-5} centimeter. Lamar and Compton consider it to occur within a space of less than 1.76×10^{-4} centimeter, and give the cathode potential drop as about 10 volts (9.9 volts).[99] An earlier value of only 5.27 volts[100] was said to have been based upon the use of an erroneous probe method. Killian[101] also found about 10 volts and Gaudenzi[102] about 9 volts. Kommnick and Lübcke[103] find quite similar values, so that the mercury arc must be regarded as a special case of a low voltage arc. It was even found possible by Hebb[104] to maintain an arc in mercury vapor at only 1.7 to 1 8 volts although the 2537 line requires for its excitation (see below) 4.9 volts. Such an abnormal arc has been studied by Bär,[105] whose arc burned at 3.5 volts at 175°C. Unlike the earlier abnormal arcs, this was not due to oscillations, but to some positive space charge maintained before the cathode. Reverse fields sometimes play a part.[106]

After discussing in detail the attempts to determine from heat balance data the fraction of the current carried by electrons and by positive ions at the cathode, Compton[107] concluded these to be futile since the range of certain quantities needed in the calculations was not known. It was, however, possible to show that the heat balance may be made consistent with Langmuir's theory and with the known facts of ionization by making certain reasonable assumptions regarding the unknown fraction of energy returned to the cathode by unelectrified carriers such as neutral atoms in various energy states, or by radiation.

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[90] Mason, R. C., *Phys. Rev*, **38**, 427 (1931); Compton, K. T, and van Voorhis, C C, *Proc Nat. Acad Sci*, **13**, 336 (1927); Compton, K. T., *Trans. Am Inst. Elec. Eng.*, **46**, 868 (1927); Seeliger, R., *Physik. Z.*, **27**, 37 (1926); Lübcke, E, *Z tech. Physik*, **10**, 598 (1929).

[91] Compton, K. T., *Phys. Rev*, **37**, 1077 (1931)

[92] Güntherschulze, A., *Z. Physik*, **11**, 74 (1922).

[93] Kobel, E., *Phys. Rev.*, **36**, 1636 (1930).

[94] Nikiforov, A. Y, *J. Exptl. Theoret Phys (U.S.S R)*, **6**, 168 (1936); *Chem Abs.*, **31**, 14 (1937).

[95] Slepian, J., *Phys. Rev.*, **27**, 407 (1926).

[96] Langmuir, I., *Science*, **58**, 290 (1923); *Gen. Electric Rev.*, **26**, 735 (1923); see also Mackeown, S. S., *Phys. Rev.*, **34**, 611 (1929).

[97] Lamar, E. S., and Compton, K. T, *Phys. Rev.*, **37**, 1069 (1931); see also Gvosdover, S. D., *Physik. Z. Sowj.*, **7**, 274 (1935).

[98] Güntherschulze, A., *Z. Physik*, **11**, 74 (1922).

[99] Lamar, E. S., and Compton, K T., *Phys Rev.*, **37**, 1069 (1931)

[100] Stark, J., Retschinsky, T., and Shaposchnikoff, A., *Ann Physik*, **18**, 213 (1905).

[101] Killian, T. J, *Phys Rev.*, **31**, 1122 (1928).

[102] Gaudenzi, A, *Brown-Boveri Rev.*, **16**, 303 (1929)

[103] Kommnick, J., and Lubcke, E., *Physik. Z*, **33**, 215 (1932).

[104] Hebb, T. C., *Phys. Rev.*, **16**, 375 (1920), see also Yao, Y. T., *Phys. Rev*, **21**, 1 (1923).

[105] Bär, R., *Z. Physik*, **31**, 430 (1925).

[106] Rudy, R., *J. Frank Inst*, **201**, 248 (1926); v. Dziewulski, H., *Z. Physik*, **69**, 366 (1931).

The cathode spot moves rapidly on the mercury surface as it becomes conditioned and migrates to a neighboring spot where the mercury surface is contaminated by impurities and where the electrons can be more readily extracted. The mercury surface becomes depressed and the electrons probably come from the irregular edge of the crater, which is then immediately depressed, due to the vapor pressure of the mercury, heated by the bombardment of positive ions at the cathode spot. This would also account for the rapid movement of the cathode spot, since the electrons always come from the edge of the crater, which is then depressed by the increased vapor pressure at that point. Tonks[108] described methods of preventing this unsteadiness at the cathode end of the positive column by the use of wires of certain metals, especially molybdenum, the cathode spot being limited to the line of wetting. From the spectral distribution of the radiations from such anchors, it was suggested that there might be a region of "hot" ionized gas close to the cathode. Cravath[109] studied the behavior of the mercury vapor arc with a jet of liquid mercury as cathode, but was unable to obtain a stationary cathode spot on the jet.

It has been found that the mercury arc can be operated with the cathode frozen at $-70°$C, the voltage being not much higher than that for the normal operation of the arc.[110] Newman[111] has also studied the operation of the mercury arc at liquid air temperatures, his experiments supporting the idea that the fraction of the current carried by electrons depends on the vapor pressure. The parts of the arc immersed in liquid air were not luminous, but there was a brilliant cathode spot.

2. *Conduction Processes in the Plasma.* Little need be added here to the general discussion of this topic given in the previous chapter. As in general in the gaseous discharge, the tension, U, on the electrodes of a mercury arc is a linear function of the arc length l, *i.e.*, $U = A + Bl$, in which A is the sum of the anode and cathode drops of potential and B is the voltage gradient in the arc. Pawlikowski[112] found the mean velocity of all electrons to be constant throughout the whole width of the positive column, although in the immediate vicinity of the cathode two groups of electron velocities were noted.

The theory of the striated glow discharge in mercury vapor was studied by Compton, Turner and McCurdy.[113] In this work, attention was drawn to the importance of cumulative ionization in the striations. This concept has since been extended to the phenomena in the ordinary discharge.

There have been many divergent statements in regard to the transfer of mercury between the electrodes of the direct-current arc. Perot,[114] who made one observation of the change in mercury levels in an inverted U-arc, believed all of the current to have been carried by univalent mercury ions. Matthies,[115] however, found no mercury transfer other than that due to thermal processes and believed the conduction to be entirely electronic. Other workers took intermediate positions. Güntherschulze [116] believed half of the current carried by electrons and half by ions and Schottky and von Issendorff,[117] that 80 per cent was carried by ions. The more recent calculations of Langmuir have shown that the positive ion current is not more than 1/340 to 1/605 of the electron current density. Tonks [118] states that of the current carried by mercury ions 50 per cent is by doubly and 12 per cent by triply charged ones.

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[107] Compton, K. T., *Phys. Rev.*, **37**, 1077 (1931); Compton, K. T., and Langmuir, I., *Rev Modern Physics*, **2**, 184 (1930). For other earlier attempts, see Güntherschulze, A., *Z. Physik*, **31**, 509 (1925); Seeliger, R., *Physik. Z.*, **27**, 22 (1927); *Elektrotech. Z.*, **49**, 853 (1927); Compton, K. T., and van Voorhis, C., *Proc. Nat. Acad. Sci.*, **13**, 336 (1927); v. Issendorf, J., *Physik. Z.*, **29**, 857 (1928). See also Gehrts, A., and Vatter, H., *Z. Physik*, **79**, 421 (1932), and Weizel, W, Rompe, R., and Schon, M., *Z. Physik*, **112**, 339 (1939).

[108] Tonks, L., *Physics*, **6**, 294 (1935).

[109] Cravath, A. M., *Phys. Rev.*, **36**, 1480 (1930).

[110] Kawa, J., *Acta. Phys. Polonica*, **1**, 427 (1932); *Chem. Abs.*, **28**, 4667 (1934).

[111] Newman, F. H., *Phil. Mag.*, **18**, 607 (1934).

[112] Pawlikowski, J., *Acta. Phys. Polonica*, **2**, 59 (1933); *Chem. Abs.*, **28**, 7155 (1934).

[113] Compton, K. T., Turner, L. A., and McCurdy, W. H., *Phys. Rev.*, **24**, 597 (1924).

Forbes and Leighton,[119] using a lamp which was too hot to allow condensation of mercury to occur on the walls, found the ratio between the gram atoms of mercury transferred from the anode to the cathode and the faradays passing through the lamp to be sensitive to cathodic cooling and that mercury can migrate against considerable temperature gradients. Extrapolation of their results to the lowest voltage gradients and pressures indicated a minimal mercury transfer and an insignificant role for the positive ions. But, as the voltage gradient and the pressure rise, the positive ion current appears to gain on the electron current. At five volts per centimeter, the ratio has reached five, almost irrespective of the current, and remains near that value up to 25 volts per centimeter and a pressure of three atmospheres. Elenbaas [120] has discussed the theory of the gradient of the high-pressure mercury discharge.

3. *The Pressure in the Arc.* Küch and Retschinsky [121] measured over twenty internal pressures in an arc 12 mm. in diameter. Between 3 and 18 volts per centimeter, the pressure rose from 38 to 1500 mm., the current varying between 4.1 and 5.05 amperes; they gave, however, no quantitative correlation between the pressure and other variables.

Forbes and Leighton,[122] realizing that the electrical conditions depend on the resistance, pressure and the efficiency of air and water-cooling, presented graphs relating the pressure to the voltage gradient for arcs of 9 and 2 mm. diameter, (see Section on Constricted Arcs, Chapter 6) each carrying various currents. They concluded

(a) The pressure is a function of the cross section, voltage gradient and current, but not of the arc length or the relative cathode and anode temperatures.

(b) In spite of wide differences in the arc cross section and the current carried, the pressure changed about 140 mm. for a unit change in the voltage gradient, and the curves became nearly parallel at pressures greater than two atmospheres.

(c) For a given lamp at constant voltage, the pressure is very roughly proportional to the logarithm of the current.

(d) At low voltage gradients, the ratio of pressure to cross section for a given current strength is nearly the same for the constricted arc as for the normal arc, but at higher voltage gradients, the ratio is greater for the constricted arc.

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[114] Perot, A., *J. Phys.* (5), **1**, 609 (1911).

[115] Matthies, W., *Ann. Physik*, **37**, 721 (1912).

[116] Güntherschulze, A., *Z. Physik*, **11**, 75 (1922); **31**, 509 (1925).

[117] Schottky, W., and von Issendorff, J., *Z. Physik*, **26**, 85 (1924).

[118] Tonks, L., *Elec. Eng.*, **53**, 239 (1934)

[119] Forbes, G. S., and Leighton, P. A., *J. Opt Soc Am*, **12**, 53 (1926). For the clean-up of mercury by the walls, Kenty, C., *J Applied Phys.*, **9**, 765 (1938)

[120] Elenbaas, W., *Physica*, **1**, 673 (1934), **2**, 757, 767, 787, 807 (1935); **4**, 279 (1937); *Phys. Rev.*, **55**, 294 (1939).

[121] Küch, R., and Retschinsky, T., *Ann Physik*, **20**, 563 (1906)

[122] Forbes, G. S., and Leighton, P. A., *J. Opt. Soc. Am.*, **12**, 53 (1926).

(e) Had there been an "anode pressure" as suggested by Hamburger,[123] and by Skaupy,[124] it would have been noted.

4. *Electrical Operating Characteristics of the Mercury Arc.* The early knowledge of this field was summed up by Buttolph.[125] The following account is based largely upon his more recent accounts.[126]

On starting the Uviarc lamp, the vapor pressure is low, as the lamp is cool, and the current is high and the voltage low. The lamp requires a short time to reach normal operating conditions, depending upon the heat capacity of the mercury cathode and arc tube, and upon the initial arc energy. As the temperature rises, the vapor pressure and the voltage follow, while the current drops. Normal operation is reached when heat is radiated from the burner at such a rate that the vapor pressure no longer rises. In the upper left hand corner of Figure 37 the change in voltage and in current which occur during the first few minutes after starting are separately plotted and show clearly the way in which the arc comes to normal operation. As the starting current and the final arc voltage are each determined by the series resistance, a family of starting curves for different values of the series resistance is given in the main portion of the figure. The locus of the terminations of these curves at operating equilibrium at 25°C., H-L, is called the stationary or static characteristic curve for that arc at that temperature.

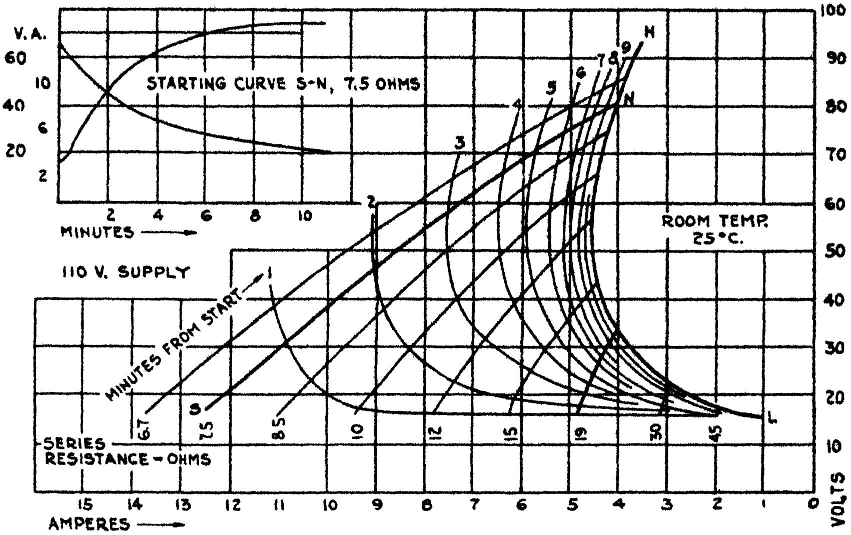

FIGURE 37. Starting and Operating Curves of Vertical Uviarc (Buttolph, *Review of Scientific Instruments*).

During the transition from the low pressure arc starting condition to the high pressure arc, there occurs a striking change in the appearance of the luminous arc column. As seen through a dark filter, the principal light source becomes concentrated in the center of the arc tube as a slender cord of great brilliancy. In this condition there is about 25 volts drop per inch in the arc as compared with approximately 1⅓ volts per inch in the low-pressure arc.

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[123] Hamburger, L., *Proc. Acad. Sci. Amsterdam*, **25**, 1045 (1917).

[124] Skaupy, F., *Verh. Deut. Phys. Ges.*, **19**, 264 (1917).

[125] Buttolph, L. J., *Gen. Electric Rev.*, **23**, 741, 858, 909 (1920).

[126] Buttolph, L. J., *Rev. Sci. Instruments*, **1**, 487 (1930); *Trans. Illum. Eng. Soc.*, **28**, 153 (1932).

The Uviarc may be operated at various arc voltages from about 20 volts up to a maximum, characteristic of each size of lamp. The static characteristic curve H-L expresses the relationship between the arc voltages and the corresponding normal current. A significant feature is the steepness of the curve. The temperature at which there is normal operating equilibrium is determined largely by the temperature of the room and the ventilation of the burner. For example, with a given maximum burner voltage determined by the line voltage and the series resistance, the current normal for the design is increased by cooling the burner, as indicated by Figure 38. It is thus evident that the temperature of operation introduces another variable. For this reason, the 220-volt horizontal Uviarc requires about 4.5 amperes at 165 volts between the electrodes when operated in open air, while its normal current when enclosed is only about 3.75 amperes at 174 volts on the arc. To secure a relatively increased intensity of radiation in the 2537A line, Uviarcs may be immersed in water to various depths depending upon the effects desired. Depending upon the temperature, the arc voltage then does not rise to more than 20 to 40 volts at 4 to 5 amperes. Wood[127] made use of this method

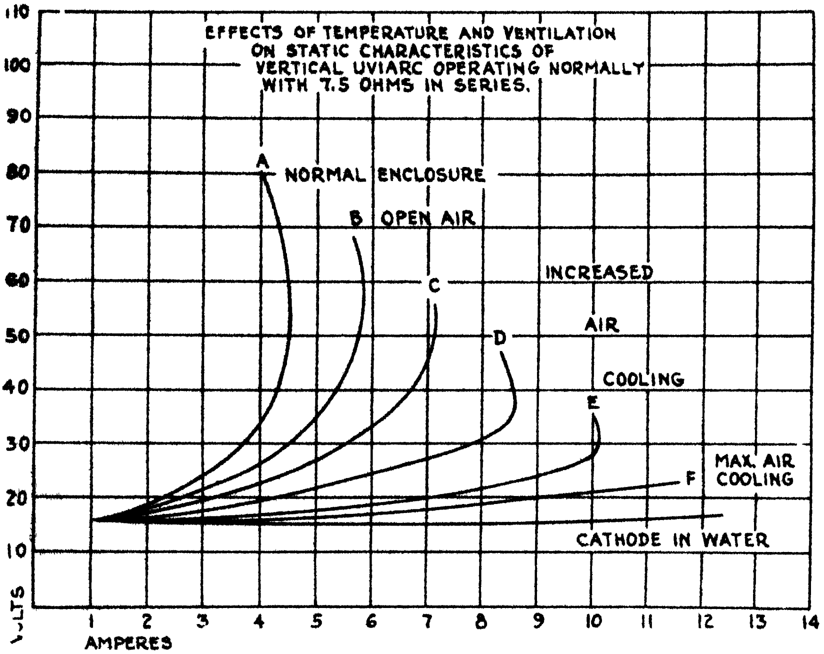

FIGURE 38. Effect of Temperature and Ventilation (Buttolph, *Review of Scientific Instruments*).

When so operated, the arc has the volt-ampere characteristic of a low-pressure arc, although the current density in the arc is greatly in excess of that obtainable under conditions of temperature equilibrium in open air. This is an inefficient operating condition. The inlead wires are not intended to carry the excessive currents which may pass. Spattering from the tungsten anode is also greater than during operation at the same current and higher vapor pressures.

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[127] Wood, R. W., *Phil. Mag.*, **50**, 761 (1925); compare also Taylor, H. S., *J. Am. Chem. Soc.*, **48**, 2480 (1926).

It is clear that the arc voltage drop depends upon the vapor pressure of the mercury, the mean vapor density of which increases with the temperature. The Uviarc dissipates about 50 watts per square inch of its silica tube, its mean temperature is about 360°C., and the vapor pressure about 800 mm. These are maximum ratings based on an economic life of 6000 hours of continuous operation.

Among the first thorough studies of the static characteristic curves of the mercury arc were those of Harrison and Forbes,[128] who clearly appreciated the possibility of following changes in voltage with constant current by altering the ventilation of the arc. They also showed the negative characteristic in certain regions of the static curve; an increase in applied voltage produces a decrease in the current. When it gets too hot the lamp goes out.

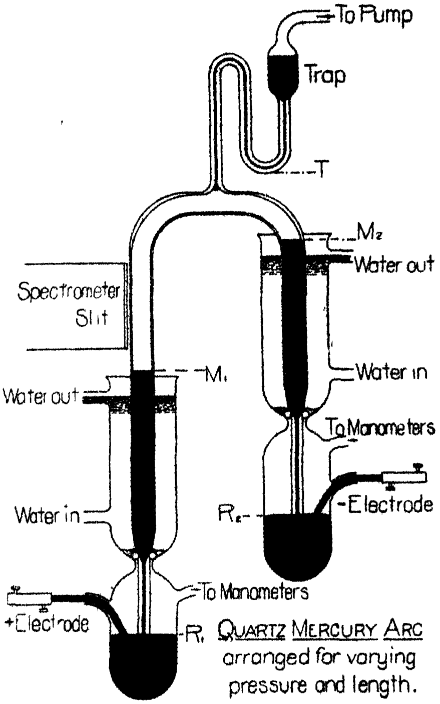

FIGURE 39.

Special Design of the Harrison and Forbes Experimental Mercury Arc (*Journal of the Optical Society of America*).

For their work on the influence of current and voltage on the spectral distributions of the radiations, they designed a special lamp with variable length. (Figure 39.) The results were reduced to unit length after deducting the electrode drop in voltage, taken as 12 volts. Legs of an inverted copper U dipped into two Pyrex reservoirs, sealed to them by de Khotinsky cement, the upper part of each serving as water-cooler and the lower containing mercury for the arc. Iron wires sealed into the sides of the reservoirs dipped almost to the bottom of the mercury pools. A quartz trap was sealed to the top of the arc, so that the last traces of air in the tube could be exhausted by boiling the mercury up into the trap. When the lower legs and trap tube were of large bore, the arc had a great tendency to oscillate, the mercury levels moving up and down several centimeters and the arc-voltage varying by 20 per cent or more. To damp the oscillations down to a few hundredths of a millimeter and to keep the voltage constant, these legs were replaced below the water-coolers by quartz capillaries of 1 mm. internal diameter, the finest thread of mercury that would carry the maximum current of 5 amperes.

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[128] Harrison, G. R., and Forbes, G. S., *J. Opt. Soc. Am.*, 10, 1 (1925).

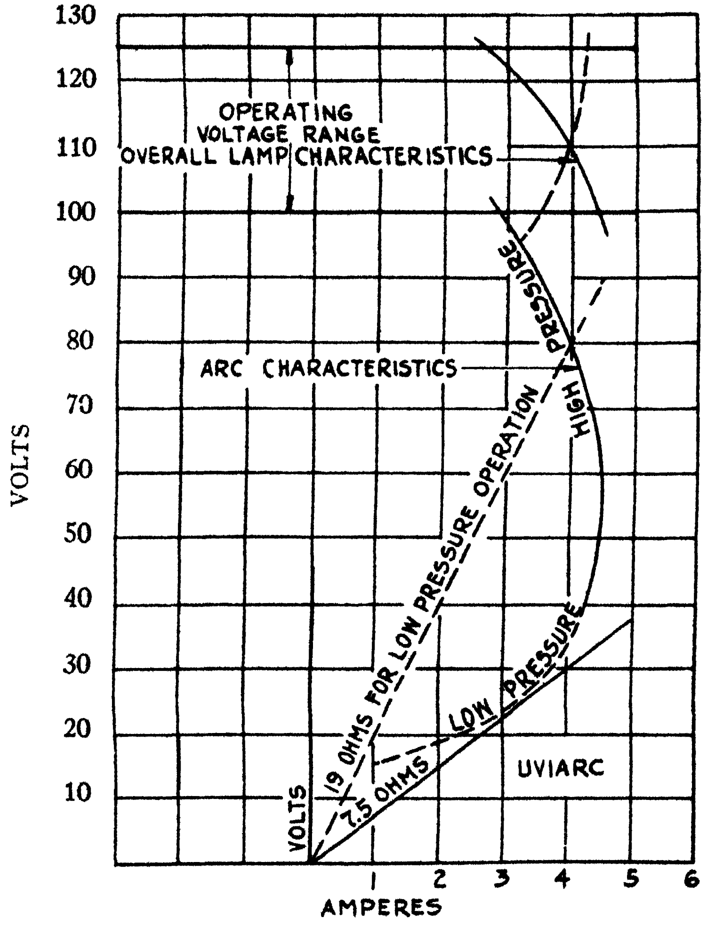

FIGURE 40. Regulation Characteristics for Slow Changes of Line Voltage (Buttolph, *Review of Scientific Instruments*).

The bands of the upper part of the tube were made with thickened walls to prevent fusion under the greater heat caused by deflected ions. The two reservoirs and trap were connected to vacuum through rubber pressure tubing by stopcocks, so that any one could be separately exhausted either through an inch of thermometer capillary or through a tube of large bore. Exact control of all mercury levels was possible. Air pressure up to two atmospheres could also be supplied to the reservoirs. Their pressures could be read from manometers.

In starting, both reservoirs and the body of the lamp were exhausted to a fraction of a millimeter and then mercury was allowed to rise slowly in the arms. The outside of the lamp was heated by a Bunsen burner and the mercury boiled vigorously. When it had risen so as to fill partly the trap, the rubber tube connecting this to the pump was closed with a pinch-cock as near the trap as possible. The current was then turned on, the upper electrode being negative. The two reservoirs were then slowly exhausted until the mercury broke at the top of the U, and the arc length then increased as the pressure was built up in the tube. The height of the mercury columns was finally adjusted by varying the resistance in series with the lamp, the rate of cooling, and the pressure in the two reservoirs. Although the upper reservoir gradually filled at the expense of the lower, the excess could be returned without extinguishing the arc. A copper tube with small holes was bent to the shape of the quartz tube and air currents were directed on the whole luminous column when necessary. With this apparatus, a change could be made from one stationary state to another on a different characteristic curve much more rapidly than in the ordinary arc. The pressure could be built up rapidly in the arc when first struck by lengthening it to 25 cm., putting a large current through it, and then shortening the column, thus building up the voltage drop. The whole arc was enclosed in a large box with holes to provide variable degrees of ventilation. In series with the arc was a fairly high inductance to damp out oscillations and a variable maximum resistance of 200 ohms capable of carrying 5 amperes. The arc was fed by a 550-volt direct current generator, run on an induction motor. In no case was the voltage drop across the arc greater than 300 volts, or 17 volts per centimeter. Langmuir[129] also developed a cooled arc for the study of the characteristics of arcs at different vapor pressures.

By combining the "static" characteristic of the arc (H-L, Figure 37) with the volt-ampere characteristic of the fixed series resistance to be employed with it, there is obtained the volt-ampere curve of the actual working combination, shown in full lines in Figure 40 The use of greatly increased resistance to secure low pressure operation of the Uviarc is also shown in broken lines. The curved line marked "high pressure" is the supply voltage less the voltage drop in the series resistance and so represents the voltage available for operation of the arc at various stable arc currents. For the arc to be stable, the slope of this curve must be such that for various line voltages the voltage available for arc operation is never less than the arc drop. Buttolph emphasizes that the arc voltage is related to the current only indirectly through its ability to change the temperature and therefore the vapor pressure of the mercury. The positive volt-ampere characteristic of the Uviarc secures good "regulation" (change of voltage with current) only for very slow changes in the supply voltage which permit the attainment of temperature equilibrium.

The practical stability characteristic of the arc is better indicated by a family of "dynamic" regulation curves, such as are indicated by the series of arrow-marked lines of Figure 41. This shows the effect of sudden changes in supply voltage so rapid as to make the immediate effect of temperature changes negligible. The arrow-marked lines show approximately what happens as a result of sudden changes in supply voltage to new voltages maintained until temperature equilibrium has been attained. Since the apparent resistance can change only with the vapor pressure, the first effect of an increase in the supply voltage is only an increase in the arc current. With the resulting temperature increase, the arc voltage increases, the series resistance voltage decreases, the current decreases and normal operation is resumed at a higher arc voltage with practically the original current. A sudden change back to the normal and original voltage results in a completion of the cycle in a manner identical with that indicated for sudden decreases from normal. For transient voltage fluctuations, this cycle becomes greatly distorted and at high frequencies finally degenerates to changes only along the line LNH. The fact that the Uviarc current only affects the arc voltage rather slowly through the arc temperature, affects its apparent static instability, the cycle shown by the lines L'N'H' requiring a relatively long time for completion. The curve marked "arc watts" shows that a condition of energy and temperature maximum exists at approximately the normal operating voltage. The "regulation" of the lamp depends upon the amount of series resistance used; this is determined by the permissible arc current fluctuation and the local variation in power supply voltage.

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[129] Langmuir, I., *Gen. Electric Review*, 27, 538 (1924).

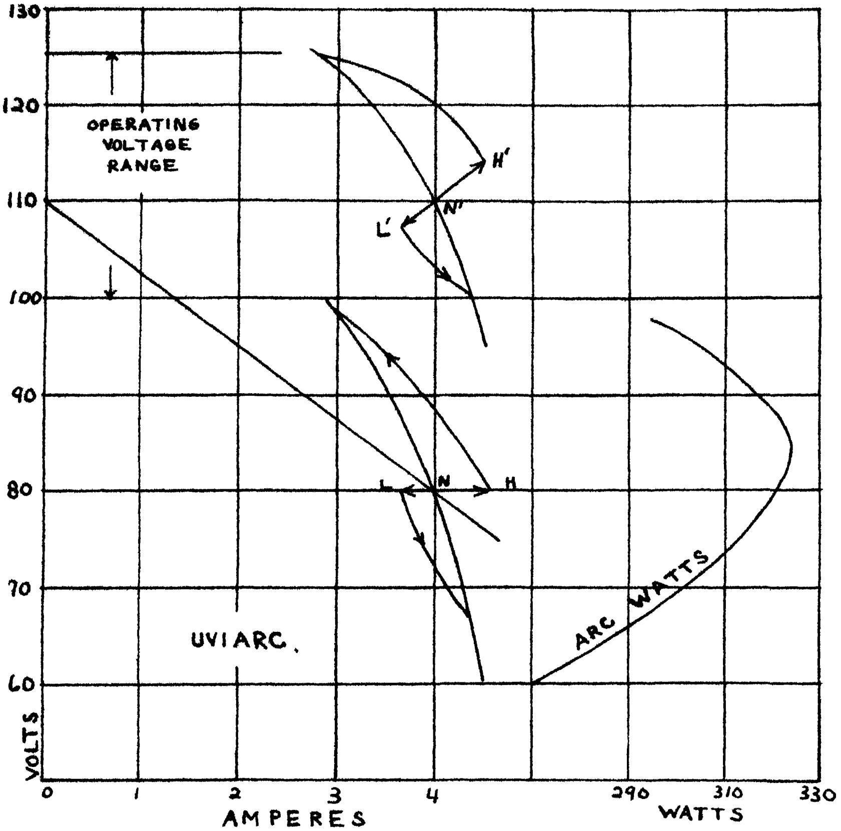

FIGURE 41. Regulation Characteristics for Sudden Changes of Line Voltage (Modified from Buttolph, *Review of Scientific Instruments*).

There is also an inherent instability of the arc, related to changes in its apparent resistance, and ascribed to transient high-frequency variations of the current. This appears to be a cathode phenomenon, the cause of which is not definitely known. These current variations are most pronounced during low-pressure operation at starting and result in an arc-extinguishing effect opposed only by the impedance of the circuit. The arc and its supply line act much like a series resonant circuit. The frequency of the oscillations may be several thousand per second; several thousand volts may be induced on the arc terminals, resulting in transient reductions of the current to amounts insufficient to maintain the arc. This form of instability may be largely eliminated by inserting sufficient resistance to absorb one-third of the supply voltage. In practice, one-quarter henry (or for a very unstable direct-current supply line or for rectifiers with pulsating output, one-half henry) in an open-core inductance connected in series with the arc and as directly as possible to the cathode, permits stable operation with about 10 per cent greater voltage on the arc than would otherwise be possible.

The arc is essentially a direct current device because the cathode cannot be maintained active on alternating current half-time operation. It may, however, be operated upon alternating current by using a rectifier circuit and an arc with two anodes. (See Figure 42.) The cathode is connected to the secondary midpoint of a transformer, and the anodes are connected to its terminals. The series resistance may be in two sections placed adjacent to the anodes, or in a single unit placed either between the arc cathode and the transformer or in series with the primary. Either the anodic or the primary positions are preferable. The mercury cathode remains continually negative relative to either one anode or the other at all times, being maintained through zero supply voltage by the cathode inductance. The electron stream passes from the cathode to one anode during the active half-cycle, to the other anode during the following half-cycle, and to both anodes during the transition. The inductance has the new function of maintaining the arc current at a level sufficient to keep the hot spot alive during zero voltage. This effect can be secured by using a transformer of sufficient magnetic leakage and even the regulating resistance can be replaced by reactance, but either of these changes causes so great a lowering of the power factor as to be impracticable. Buttolph[130] gives a detailed analysis of typical oscillograms, which lies beyond the scope of this book.

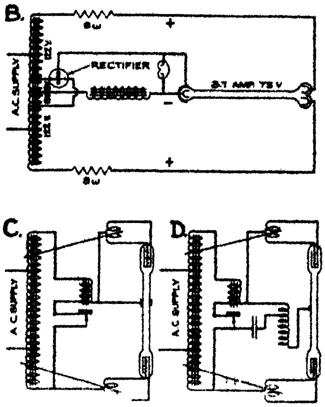

FIGURE 42.

Circuits for Alternating Current Mercury Arc (Buttolph, *Transactions Illuminating Engineering Society*).

The starting of the alternating-current arc is complicated by the fact that the starting circuit is, in effect, connected to but one of the two anodes, and that the current flowing in the shifter circuit is alternating and hence is of the correct polarity for arc starting but one half of the time. A further limitation to the use of this method in the starting of the alternating-current rectifier type of arc lies in the fact that to secure a satisfactorily high induced potential, the negative inductance or choke must be of so high a value that a potential of about 120 volts must be applied to the starting circuit in order to secure a satisfactory shifter current. This causes great stability in the shifter arc, resulting in a trailing of the shifter arc through to the extreme end of the half cycle in which the mechanical break occurs. Figure 42B shows a solution of several of these problems[131] through the use of a small dry rectifier supplying about one ampere of rectified direct current of just sufficient voltage to cause a flow of about one ampere through the inductance. The impedance of even one-third henry choke to this pulsating direct current is so low that the equivalent of only about a three- or four-volt direct current supply is required to secure a shifter current of over one ampere.

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[130] Buttolph, L. J., *Rev. Sci. Instruments,* **1,** 500 (1930).

[131] Buttolph, L. J., *Trans. Illum. Eng. Soc.,* **28,** 153 (1932).

Other starting methods as a choke and either a mercury switch or a mechanically operated circuit-breaker may be used to secure high voltage transients sufficient to ionize the gas and start the discharge in the ordinary type of alternating current arc. (Figure 42C.) An alternative to the relatively slow action of a mercury interrupter or of a mechanically vibrating interrupter is the use of a simple oscillatory circuit (Figure 42D) in which there is imposed on the arc tube a high-voltage, high-frequency impulse, the high-frequency nature of the discharge being effective through the use of an external electrode placed preferably somewhere near the center of the arc tube.

A detailed treatment, based upon studies with the oscillograph, has been given by Buttolph and Dana.[132]

THE MECHANISM OF THE EMISSION OF RADIATION

The radiation emitted by the Uviarc extends from the 10,140A [133] line in the infrared to the region of 1850A in the ultraviolet. The energy-level diagram of mercury given in Figure 4 (Chapter 2) forms the basis for an interpretation of the lines emitted in terms of the impacts of electrons possessing the necessary kinetic energies. The connecting lines between the various energy states represent most of the lines of the arc spectrum of mercury. It has been stated in the preceding section that very small fractions of the current are carried by ions of valence higher than one. The presence of such ions makes it possible that some of the lines of the emission spectrum of the mercury lamp may be ascribed to transitions which would find their representations on other energy level diagrams for the corresponding ions; these are, however, of little significance.

The diagram indicates that the two resonance states produced by impacts of 4.87 and 6.67 electron-volts produce lines in the ultraviolet at 2537 and 1849A, respectively. The various visible lines are produced by transitions from higher energy levels to the lowest excited levels corresponding to the resonance potentials or to a metastable state.

The metastable states of the mercury atom are energy levels from which there occur no transitions with emission. The diagram indicates that 7.7 volts (applied in two stages) produces an energy level 2^3S_1, from which the green line 5461A is emitted, the atom falling into a metastable state, 2^3P_2. A second metastable state, 2^3P_0, is produced similarly by a transition from the 2^3S_1 state with emission of the 4047A line. While the usual higher energy level states have a duration of about 10^{-8} second, the metastable states persist for times of the order of 10^{-3} to 10^{-4} second.[134] The metastable states can also be reached from the normal states by direct electron impacts, but the direct transition from a metastable to a normal state is very improbable, so much so that the lines corresponding to such transitions are "forbidden" lines. Various processes limit the existence of an atom in a metastable state. Another electron can hit it and raise it to a higher energy level or even ionize it. It may suffer impact with another atom and gain or lose energy thereby. In the presence of a gas with a lower resonance or ionization potential, the metastable atom may yield some of its energy to one of the foreign atoms, raising it to a higher energy level or ionizing it.

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[132] Buttolph, L. J., and Dana, D. W., *Rev. Sci. Instruments*, 4, 209 (1933). Note also Kelting, R. C., U. S. P. 2,152,998, Apr. 4, 1939.

[133] For the infrared arc spectrum of mercury, see Wiedermann, G., and Schmidt, W., *Z. Physik*, 106, 273 (1937); Murakawa, K., *Z. Physik*, 108, 168 (1938).

[134] Methods for the determination of these life periods for various energy level states lie beyond the scope of this book. See Mitchell, A. C. G., and Zemansky, M. W., "Resonance Radiation and Excited Atoms," Cambridge, 1934.

Since in the operation of the usual forms of the mercury arc all the arc lines are emitted in addition to the resonance lines, the conditions must be such as to enable the bombarding electrons to raise the mercury atoms to the energy level corresponding to the ionization potential of 10.4 volts, although the voltage drop at the cathode by which the electrons are accelerated is only about 10 volts. Compton[135] suggested that the ionization must be produced as a result of two impacts. The electron energy is close to that required for the production of metastable atoms (see Figure 4) or to ionize these when formed.

The intensity of a line depends upon the fraction of the atoms in process of transition from a higher to a lower state; this depends upon the concentration of higher state atoms. This in turn varies directly with the electron current and the concentration of the atoms in the lower state, that is, with the current and pressure. Furthermore, the velocity of the electron must be sufficient to effect the transition in question; this depends on the voltage gradient in the region in which the electron acquires its velocity. For forming the 2^1P_1 state of mercury (6.67 volts), the probability of excitation increases from zero at 6.67 volts to a maximum at 6.8 volts, after which it decreases.[136] Similar considerations apply to each of the other states; the varying probabilities of excitation to each of these states under operating conditions accounts for the varying intensities of the lines which correspond to transitions from these states.

The theory is, however, much more complex, since the intensity of a line depends not only on the probability of formation of the necessary energy state, but also upon the probability of the transition from that state. This is true since other transitions from that state producing other lines may also occur. In place of dropping to one of several lower excitation states with emission of the corresponding lines, it may also be raised to a still higher state of excitation by suffering impact with an electron. The further analysis of these probabilities of emission, collision or ionization depends upon the determination of the mean free paths of the atoms and of their effective radii for collisions.

The uniformity of the light emitted along the lengths of the positive column shows that the electrons must acquire energy from some source other than the cathode fall. It comes from the energy input into the column, the product of the arc current into the voltage gradient. The latter factor depends upon the current density and the pressure. Schottky[137] believed the voltage gradient to vary inversely with the tube diameter. For mercury vapor, Güntherschulze[138] found at different pressures that the gradient is a function of the tube diameter, d, and the current I, $X = \frac{c}{d^a I^b}$, a, b, and c being constants. The values of a and b vary with the pressure of the mercury vapor. At 100°C., a is 0.69 and b is 0.12.

Within the positive column, the average kinetic energy of the electrons is too low to excite or ionize the mercury atoms. There is, however, a Maxwellian distribution of the kinetic energy among the electrons, so that a small fraction of them do have a sufficient amount of energy to produce these effects. The average kinetic energy (3/2 kT_e) depends upon the electron temperature T_e. Killian[139] studied the effects of pressure upon the electron temperature and total electron concentration over a low pressure range in a mercury arc in a tube of 6.2 cm. diameter, carrying a current of 5 amperes. The electron temperature decreased from 38,000°K. at 0.00020 mm. to 19,900°K. at 0.00533 mm. An electron temperature of 19,900° means that the average kinetic energy of the electrons is 2.56 volts. The fraction of the electrons having kinetic energies greater than the ionization potential of mercury is in this case, from the Maxwell-Boltzmann distribution law, about 0.003.[140] The energy lost by this small fraction of the electrons in ionizing collisions is supplied by the energy input into the positive column. Killian found also that an increase in pressure increased the probability of collisions, although it reduced the electron temperature. These opposing effects cause the emission at constant current density to pass through a maximum as the pressure is increased. Other observations showed that the electron temperature tends to decrease somewhat with an increase in the arc current. In Killian's experiments, the average electron concentrations varied between 3.7×10^{10} and 15.2×10^{10} per cubic centimeter as the pressure was increased from 0.00020 mm. to 0.00533 mm. The theory of Tonks and Langmuir[141] indicates that there is also a concentration gradient for electrons from a maximum along the axis of the tube toward the walls. Not all of the energy input into the positive column is utilized in excitation or ionization. Some of the energy is delivered to the walls, being liberated there by the recombination of electrons and ions. As the electron temperature was decreased from 38000°K. to 19,900°K. in the experiments of Killian the energy delivered to the walls by recombination processes could be calculated to decrease from 48 to 14 per cent of the total input. The remainder was available for excitation processes.

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[135] Compton, K. T., *Phys. Rev.*, **37**, 1077 (1931); see also Mason, R. C., *Phys. Rev.*, **38**, 427 (1931); Gehrts, A., and Vatter, H., *Z. Physik*, **79**, 421 (1932); Barnes, B. T., and Adams, E. Q., *Phys. Rev.*, **53**, 545, 556 (1938); Fabrikant, V. A., Butaeva, F., and Tsirg, *Physik. Z., Sowjetunion*, **13**, 23 (1938); *Chem. Abs.*, **31**, 8352 (1937); **32**, 4871 (1938).

[136] Brattain, W. H., *Phys. Rev.*, **34**, 474 (1929).

[137] Schottky, W., *Physik. Z.*, **25**, 342, 635 (1924).

[138] Güntherschulze, A., *Z. Physik*, **41**, 718 (1927); **42**, 763 (1927) (glow discharge). See also Elenbaas, W., *Physica*, **5**, 568 (1938); *Chem. Abs.*, **32**, 7340 (1938).

These experiments do not apply directly to the usual types of mercury arc, since the pressure range is quite different. Lübcke[142] finds that the electron temperatures are 7000 to 40,000°K. in the more usual forms.[143]

CONTINUOUS AND BAND SPECTRA IN THE MERCURY ARC

The line spectrum of mercury is superposed upon a fainter continuous spectrum, emitted by glowing vapor distilling from the arc. It has been in part attributed to incandescence. The continuous spectrum, together with the selective absorption of the luminous mercury vapor for its own radiation, in part accounts for a shift in the relative radiation intensity toward the longer wave-lengths with increased energy input, in contrast with Wien's displacement law. A review of continuous emission spectra in general has been given by Finkelnburg.[144]

Volkringer[145] observed a large band at 3360A and a smaller one with a maximum at 2650A. Dawson and Crew[146] found band maxima in the arc at atmospheric pressure, excited by high voltage and low current density, at 4500, 3300 and 2550A. No continuous radiation was emitted in the region 2535 to 2350A. On increasing the current, the bands broadened in both directions and filled this gap. Crew and Thornton[147] attribute the bands to the Hg_2 molecule produced at the distilling surface of the mercury and readily dissociated even by slowly moving electrons or ions. From the intensity of the band at 2540A at various temperatures and pressures, Koernicke[148] calculated the heat of dissociation of the molecule to be 1.4 kcal. Nakamura[149] regarded the 2536A band as due to the arc type of excitation of the neutral molecule and the band at 2540A as due to the ionized molecule Hg_2^+.[150]

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[139] Killian, T. J., *Phys. Rev.*, **35**, 1238 (1930).

[140] For further details of such calculations, see Dushman, S., *Elec. Eng.*, **53**, 1204, 1283 (1934).

[141] Tonks, L., and Langmuir, I., *Phys. Rev.*, **34**, 876 (1929).

[142] Lübcke, C., *Z. tech. Physik*, **14**, 298 (1933)

[143] For further details of probe tests in various mercury arcs, see Lübcke, C., *Z. tech. Physik*, **8**, 445 (1927); Gvozdover, S. D., and Konovalov, F., *Compt. rend. acad Sci. U.R.S.S.*, **1**, 553 (1934); *Chem. Abs.*, **28**, 4975 (1934); Togo, S., *J. Inst. Elec. Eng. Japan*, **53**, 109 (1933); Klyarfel'd, B., and Plokhotzkii, E., *Z. tech. Physik (U.S.S.R.)*, **5**, 796 (1934); *Chem. Abs.*, **29**, 673 (1935).

[144] Finkelnburg, W., *Physik. Z*, **31**, 1 (1930). See also Rompe, R., Schulz, P., and Thouret, W., *Z. Physik*, **112**, 369 (1939); Unsöld, A., *Ann. Physik*, **33**, 607 (1938).

[145] Volkringer, H., *Compt. rend.*, **185**, 60 (1927).

[146] Dawson, L. H., and Crew, W. H., *J. Opt. Soc. Am.*, **17**, 261 (1928).

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[147] Crew, W. H., and Thornton, W. N., *J. Opt. Soc. Am.*, **19**, 358 (1929).

[148] Koernicke, E., *Z. Physik*, **33**, 219 (1925).

[149] Nakamura, G., *Mem. Coll. Sci. Kyoto*, **10**, 1 (1926); *Chem. Abs.*, **21**, 1755 (1927).

[150] For recent studies of the origin of the mercury bands, see Lord Rayleigh, *Nature*, **119**, 423, 778 (1927); **127**, 125, 854 (1931); *Proc. Roy. Soc.* **116A**, 702 (1927); **119A**, 349 (1928); Kuhn, H., *Naturwiss.*, **16**, 352 (1928); *Z. Physik*, **72**, 462 (1931); Ponte, M., *Compt. rend.* **186**, 633 (1928); Winans, J., *Nature*, **121**, 863 (1928); Pienkowski, S., *Bull. intern. Acad. Polonaise*, Nos. 4-5A, 171 (1928); *Chem. Abs.*, **23**, 2103 (1929); Dziedzicki, N., *Compt. rend. soc. polonaise Phys.*, **3**, 207 (1928); *Chem. Abs.*, **23**, 5095 (1929); Hulubei, H., *Compt. rend.*, **193**, 154 (1931); Hamada, H., *Phil. Mag.*, **12**, 50 (1931); Winans, J., *Phys. Rev.*, **37**, 897, 902 (1931); **39**, 745 (1932); **42**, 800 (1932); Okubo, J., and Matsuyama, E., *Nature*, **129**, 653 (1932); *Science Repts. Tohoku Imp. Univ., 1st series*, **22**, 383 (1933); *Chem. Abs.*, **27**, 5642 (1933).

Chapter 7

Output of the Mercury-vapor Lamp Under Various Operating Conditions

METHODS OF MEASURING THE INTENSITY OF THE RADIATIONS

The evaluation in absolute energy units of the radiations in various lines or wave-length regions emitted by a radiation source is difficult and requires means for the isolation of various wave-length bands by filters or monochromators as well as means for measuring the energies radiated within these bands. To avoid the difficulties involved and the apparatus required for such measurements a number of workers have described photochemical reactions which indicate the effectiveness of a radiation source for conducting photochemical changes. Many of these reactions are of little value, and even the better ones require a critical understanding of all the physical factors involved if they are to be employed effectively.

Among the apparati used for measuring the quantity of radiant energy are thermopiles. When it is desired to express the results in absolute units of energy, the thermopiles must be calibrated against some standard source of energy. Thermopiles are non-selective and measure radiant energy of any wave-length. Their use is described in the following references, those by Coblentz giving detailed directions [1] for the construction, installation and use of these instruments. More recent descriptions have been given by Strong [2] and Cartwright [3]; precautions in the use of these instruments have been given by Leighton and Leighton.[4]

Mere exposure of a thermopile to a source gives information only as to the total energy emitted, but tells nothing of the distribution of radiations among the various spectral regions. To measure distribution in the ultraviolet region a quartz monochromator, by means of which the wave-lengths can be separated into very narrow bands, is frequently employed with the thermopile.[5] When using thermopiles with quartz monochromators, correction should be made for slit width,[6] aberrations, reflection, absorption, and scattering in the optical train. McAlister [7] has described in detail the use of two quartz monochromators for determining absolute ultraviolet intensities by the aid of vacuum thermopiles and Photronic cells.

It is possible, however, to obtain information regarding the spectral distribution of the energy emitted by a source, by employing filters for delimiting various ultraviolet regions.[8] Such methods are illustrated in the work of Gillam and Morton discussed below in connection with chemical actinometers. Stockbarger and Burns[9] have reported methods for standardization of the conditions to be met in the use of filters, which methods are discussed in more detail in Chapter 10. In general, the infrared energy, the energy in successively shorter-wave regions of the visible and the energy in the ultraviolet range are measured in successive experiments with the corresponding filters. The energy introduced in each of the increments is calculated by differences. The equivalent wave-length range of the increments is approximated from the filter transmission curves.[10] Fabry and Buisson[11] measured the total energy L transmitted by n different filters, of thickness d (or n different thicknesses of the same filter). They solved n equations of the form $L = A_1 e^{-m_1 d}, \ldots. A_n e^{-m_n d}$ for $A_1 .. A_n$, the n monochromatic intensities of the original source; $m_1 \ldots. m_n$ were determined separately for each filter.[12]

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[1] Coblentz, W. W., *Bur. Standards Bull.* **4**, 391 (1908); **9**, 7 (1913); Moll, W. J., and Burger, H. C., *Z. Physik*, **32**, 575 (1925); Coblentz, W. W., *J. Opt. Soc. Am.*, **5**, 259 (1921); Voege, W., *Physik. Z.*, **22**, 119 (1921).

[2] Strong, J., *Rev. Sci. Instruments*, **3**, 65 (1932).

[3] Cartwright, C. H., *Rev. Sci. Instruments*, **3**, 73 (1932).

[4] Leighton, P. A., and Leighton, W. G., *J. Phys. Chem.*, **36**, 1882 (1932).

[5] For a critical discussion, see Forbes, G. S., Report of the Committee on Photochemistry of the Division of Chemistry and Chemical Technology of the National Research Council, *J. Phys. Chem.*, **32**, 491 (1928).

[6] Coblentz, W. W., Dorcas, M. J., and Hughes, C. W., *Bur. Standards Sci. Paper*, **21**, 535 (1927); Coblentz, W. W., *Bur. Standards Bull.* **10**, 41 (1914); **17**, 1 (1920); Franklin, R. G., Maddison, R., and Reeve, L., *J. Phys. Chem.*, **29**, 713 (1925).

[7] McAlister, E. D., *Smithsonian Miscellaneous Collections*, **87**, No. 17 (1933).

Also, photoelectric cells have been used for energy measurements. Such cells have almost linear intensity-current curves, and are free from time-lag, fatigue and deterioration. Their use, however, requires a knowledge of the sensitivity regions of the various cells, since these cells are selective in their response to particular wave-length regions. When the measurement is intended to serve as an indication of the suitability of a source for effecting a given photochemical change, the wave-length region necessary to bring about the reaction must be known in order that the appropriate photo-cell may be selected.

Elster and Geitel[13] used a zinc sphere for measuring ultraviolet radiation through photoelectric effect. Szillard used cadmium in the cathode of a photoelectric cell sensitive to the region 2950 to 3900A. Griffith,[14] by employing a quartz window to the above cell, made it sensitive to 2000A and with Taylor[15] adapted it to the photometry of therapeutic lamps. Harris[16] replaced the electrometer or gold-leaf electroscope used in conjunction with such cells by more robust measuring apparatus. He adapted a thermionic valve and microammeter to a circuit employed for the measurement of the output of a quartz mercury arc. Miethe and Stenger[17] used a silver film, and Anderson[18] has described a method of measuring and controlling the total ultraviolet output from a quartz mercury arc by using the Weston "Photronic" light-sensitive cell.

An ultraviolet light meter described by Rentschler[19] comprises special uranium, thorium, cerium, titanium and tantalum photoelectric cells connected to a glow relay tube. The latter consists of an iron cathode, a thorium starting anode and a main anode contained in an inert gas atmosphere. The intensity of incident radiations is proportional to the rate at which an electromechanical counter actuated by the glow tube registers. The total energy is measured by a recording meter. Cerium is photo active below 4500A, thorium below 3700A, uranium below 3200A, titanium between 2700-3200A, and tantalum between 2000-3000A. A proper choice of metal and quartz or glass container allows radiations of definite wave-length bands to be measured. It has been employed, with some modifications, in the investigations on air pollution conducted at the Mellon Institute.[20] Figure 43 shows the wiring diagram of the Rentschler Ultraviolet Meter.[21] The photoelectric cell shown on the central panel is mounted in a special glass bulb which admits all the ultraviolet reaching the surface of the earth. It has two electrodes, a central rod and a cathode of uranium, sputtered (in argon) over a small area of approximately 12 square centimeters on the inside wall of the bulb.

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[8] See Krefft, H., and Rössler, F., *Z. tech. Physik*, **17**, 479 (1936).

[9] Stockbarger, D. C., and Burns, L., *Phys. Rev.*, **34**, 1263 (1929).

[10] Coblentz, W. W., Long, M. B., and Kahler, H., *Bureau of Standards Bull.* **15**, No. S 330 (1918).

[11] Fabry, C., and Buisson, H., *Compt. rend.*, **152**, 1839 (1911).

[12] Coblentz, W. W., and Kahler, H., *Bur. Standards Bull* No. 378 (1920). Ornstein, L. S., *J. phys. radium (7)*, **4**, 613 (1933). Kawa, J., *Towarzystwa Fiz*, **4**, 27; *Chem. Abs.*, **25**, 2361 (1931).

[13] Elster, J., and Geitel, H., *Physik. Z.*, **12**, 609 (1911); **13**, 739, 852 (1912).

[14] Griffith, H. D., *Lancet*, 5th December, 1205, 1925.

[15] Griffith, H. D., and Taylor, J. S., *J. Hyg.*, **25**, 218 (1926).

[16] Harris, D. T., *J. Sci. Instruments*, **6**, 2 (1929).

[17] Miethe, A., and Stenger, E., *Z. wiss. Phot.*, **19**, 57 (1919).

[18] Anderson, W. T., Jr., *Rev. Sci. Instruments*, **5**, 127 (1934).

[19] Rentschler, H. C., *J. Am. Inst. Elec. Eng.*, **49**, 113 (1930); see also U. S. P. 1,923,844, August 22, 1933.

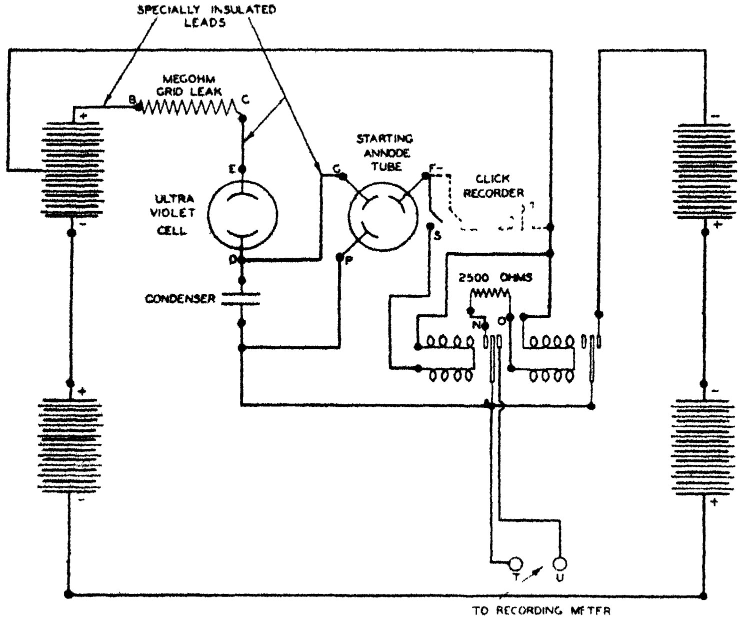

FIGURE 43. Wiring Diagram for Ultraviolet Meter (Meller, Hibben and Warga, *Transactions Illuminating Engineering Society*).

The uranium cathode, by emitting electrons, allows current to flow through the cell only when radiations between 2700 and 3350A fall upon it. The current is proportional to the intensity of the radiation, but is very small (0.1 microampere) and requires amplification by a glow relay or starting anode tube. The current trickling through the cell slowly charges a condenser. When this reaches a fixed value, the condenser spills over and an impulse of current flows between its plates. The frequency with which this occurs is proportional to the intensity of the radiation. The current flow in the tube at this point operates either a click recorder or a graphic recording meter in which a moving pen integrates the impulses over a short time interval. The record discloses variations that may occur rapidly. The sensitivity of the uranium photo-cell, shown in Figure 44, is at a maximum between 2950 and 3000A. Different cells have different sensitivities and each cell must be calibrated. According to Meller, Hibben and Warga, the chief source of error is leakage to the ground or around the condenser. They calibrated their meter against a standard tungsten-ribbon lamp which, operated at 27.5 amperes, had a true temperature of 2800°K. The results are given in arbitrary units, the number of impulses per unit of time.

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[20] Meller, H. B., Hibben, S. G., and Warga, M. E., *Trans. Ill. Eng. Soc.*, 27, 64 (1932).

[21] Rentschler, H. C., and Henry, D. E., U. S. P. 1,815,073, July 21, 1931; British P. 353,981, June 12, 1929; Rentschler, H. C., U. S. P. 1,871,280, Aug. 9, 1932; 1,917,854, July 11, 1933; British P. 353,554 and 353,555. Special fluorescent filters for use in conjunction with such photocells have been described by E. D. Wilson, U. S. P. 2,128,110, Aug. 23, 1938; *Chem. Abs.*, 32, 7824 (1938).

Dorno [22] also finds the cadmium cell to be sensitive between 2800 and 3500A. Coblentz and Stair [23] described a portable ultraviolet intensity meter comprising a photoelectric cell, balanced amplifier, and microammeter.[24] Coblentz [25] developed a practical field method for determining the energy distribution of the sun in absolute units. Two methods were devised, one employing filters and a balanced thermopile calibrated in absolute value against a standard of thermal radiation. The other employed a titanium photoelectric cell calibrated in absolute value against a standard of ultraviolet radiation. For the latter, Coblentz and Stair [26] use a commercial vertical mercury-in-quartz arc.[27] It proved of especial value

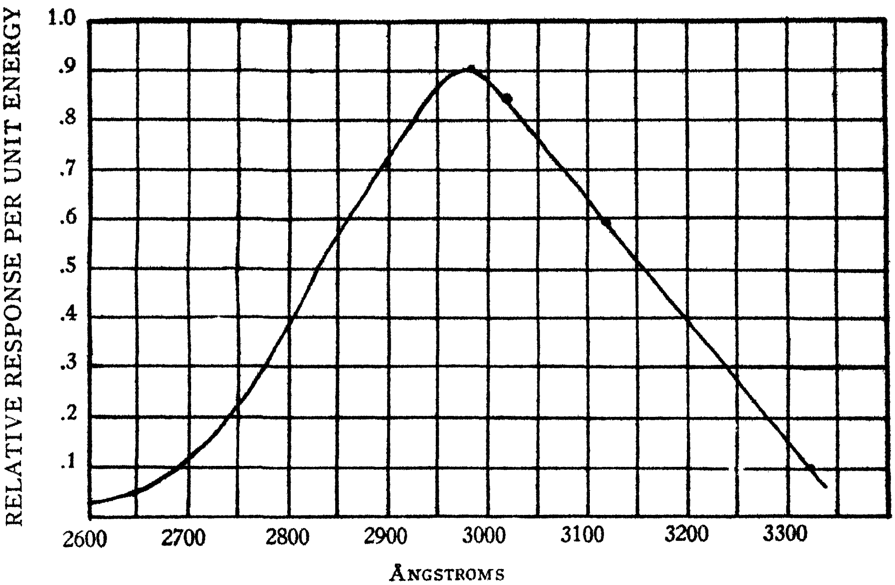

Figure 44. The Response or Sensitivity Curve of the Ultraviolet Photocell (From Meller, Hibben, and Warga, *Transactions of Illuminating Engineering Society*).

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[22] Dorno, C., *Strahlentherapie*, **25**, 361 (1928); *Chem. Abs.*, **22**, 1540 (1928).

[23] Coblentz, W. W., and Stair, R., *Bureau Standards J. Research*, **12**, 231 (1934).

[24] For further discussion of the calibration of photoelectric cells, or for the use of thermopiles and filters in measuring the energy distribution of sources, see Coblentz, W. W., *Science*, **76**, 412 (1932); *Strahlentherapie*, **50**, 179, 487 (1934); *Am. J. Roentgenol. Radium Therapy*, **33**, 793 (1935); Coblentz, W. W., Stair, R., and Hogue, J., *Bur. Stand J. Res.*, **7**, 723 (1931); **8**, 759 (1932); Coblentz, W. W., *Bull Bureau Stand.*, **9**, 51 (1912); **11**, 87; *Bur. Stand. J. Res.*, **11**, 79 (1933).

[25] Coblentz, W. W., *Puerto Rico J. Public Health Trop. Med.*, **11**, 1 (1935); *Chem. Abs.*, **30**, 118 (1936).

[26] Coblentz, W. W., and Stair, R., *J. Res. Bur. Standards*, **16**, 83 (1936).

[27] Report of the Illuminating Engineering Society Subcommittee on the Measurement of Ultraviolet Radiation, *Trans. Illum. Eng. Soc.*, **28**, 864 (1933).

as a standard for meters used to evaluate sources for germicidal and erythema-producing effects by the aid of the photo-cell. Since the cell is insensitive to wave-lengths longer than about 3300A, and since the short-wave response may be limited to about 2800A by enclosing the cell in Corex D glass, practically only the strong emission lines at 2967, 3024 and 3132A are effective. A gas-filled tungsten lamp has been employed occasionally as a standard, but a source emitting a continuous spectrum has several disadvantages over the discontinuous spectrum of the mercury arc.

One method of calibrating a photoelectric intensity meter in absolute values comprises observing the microammeter reading on exposure of the cell to a strong emission line of the mercury arc, *e.g.*, 2967A, the energy value of which had been determined in absolute units. By dividing the scale reading by the efficiency of the photoelectric response for that wave-length, the true scale reading would be relatively the same as that of a spectrally nonselective radiometer. For reasons concerned with the construction of the photoelectric cell first employed by Coblentz, difficulties were encountered in attempting to operate it at the exit slit of the spectroradiometer used in isolating the 2967A line. Therefore, it proved simpler to use the arc with a Corex D filter, so that the radiations effective on the photocell were limited (as before mentioned) to a few lines. The sum of these emissions could be accurately evaluated in absolute units with a balanced thermocouple and filters at the time the photoelectric measurements were made. Comparative reading would be taken at the same distance from the lamp in both instances. This obviates the effect of room temperature upon the output of the standard source. Alternatively, the lamp could be operated at a constant energy input in an inclosure maintained closely at the same air temperature, so that a single standardization of the lamp against the thermopile suffices until the lamp shows signs of ageing. This ageing (a blackening of the tube surrounding the tungsten anode) is eliminated, together with flickering at the cathode, by placing an aluminum diaphragm in front of the lamp to limit the emission to 30 millimeters at the central portion of the lamp. The lamp employed was the Cooper-Hewitt, 110-volt, vertical Uviarc mounted in a support which permits tilting the burner to a horizontal position for starting. A laboratory rheostat of about 18 ohms was connected in series. The potential was kept at about 5 volts below normal (70 volts) to decrease depreciation. The lamp and mounting may be kept in a ventilated, galvanized housing. When used with the diaphragm, the apparent depreciation is slow. Operated on a storage battery, the lamp remains constant at 65 ± 0.3 volts. This slow fluctuation of ± 0.3 volt is probably the result of changes in ventilation and is easily controlled with a rheostat, so that the ultraviolet output in a particular region is regulated within two or three parts in 1500.

Gyemant[28] described a fluorescent intensimeter for ultraviolet rays. A simple "UVscope" described by Alexander and referred to by Moss and Knapp was a filter of Chance's glass which absorbed all rays shorter than 3650A, the longer transmitted rays being recorded by their effects on photographic paper. The Hanovia Co.[29] described an apparatus with a fluorescent screen and ammeter indicator from which the intensity of the light could be directly read.

The Geiger-Müller electron counter, widely used in cosmic ray measurements, has been employed for the measurement of an ultraviolet beam, by counting the electrons produced by the photoelectric effect of the beam. The counter is used chiefly in the study of ultraviolet of very low intensities, such as the assumed mitogenetic rays.[30]

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[28] Gyemant, A., *J. Opt. Soc. Am.*, 12, 65 (1926).

[29] Croad, A. K., British P. 320,794, Nov. 8, 1928, to The Hanovia Co.; *Brit. Chem. Abs.*, B, 1021 (1929).

Chemical Actinometers. Comparison of some chemical actinometers was given by Eidinow.[31] Since the reactions depend upon the intensity of restricted wavelength regions, the results of such measurements may show apparent disagreement. In using chemical methods as a rough guide to the times of exposure required for a given reaction to be effected by a lamp, it is essential to select a test reaction which is effected in approximately the same wave-length region as that required for the reaction to be conducted. This is true since every photochemical reaction has its own characteristic curve of spectral sensitivity, while every light source has its own spectral energy distribution. Thus for controlling the bactericidal action of a lamp, it is necessary to choose as a test reaction one which is not effected by visible radiations or by those longer than about 2950A. (See Chapter 35.) Dorcas and Forbes[32] pointed out the necessity of using in conjunction with a chemical actinometer, a filter which transmits for each wavelength a fraction of incident radiation proportional to the efficiency of the radiation in promoting the reaction for which the light is intended to be employed. This method of measurement furnishes a comparison of the abilities of sources of different spectral distribution to effect a given reaction. In the case of skin erythema tests, taken as an index of biological stimulation, a filter comprising a one-centimeter thickness of 0.00025 molar picric acid between a sheet of red-purple Corex glass 2.5 mm. thick and one of clear Corex was utilized. This filter had an absorption curve bearing a resemblance to the Hausser and Vahle erythema curve[33] replotted on the basis of quanta rather than ergs. The replotting was done by multiplying the ordinates of the Hausser and Vahle curve by numbers inversely proportional to the corresponding wave-lengths. As the actinometric reaction, Dorcas and Forbes selected the photolysis of *p*-benzoquinone in 50-per cent alcohol, a reaction which absorbs completely the light transmitted by the filter. This reaction, which had been studied by P. A. Leighton, satisfies the necessary condition of having a practically constant quantum yield (See Chapter 12) between 3130 and 2540A. Each wave-length transmitted through the filter may be assumed to photolyze a mass of quinone proportional to the erythema-producing power of the corresponding light component of the original source. The irradiation period was two hours. A second sample was kept in a dark vessel for the same period as control. Both samples were then cooled in ice, and titrated simultaneously with 0.004*N* thiosulfate, adding 10 cc. of normal iodide and of 1.5 normal hydrochloric acid at the start, with starch indicator. It was assumed that all of the monochromatic effects for this reaction could be integrated by summation since the reaction has no induction period and only a few per cent of the reaction material is decomposed, so that absorption by reaction products does not interfere. A plot of the milligrams of quinone decomposed per hour by a series of differently cored carbon arcs against the reciprocals of the times required for the production of a standard erythema indicated a fair degree of proportionality. As such proportionality implies that the reciprocity law holds for both reactions (erythema and photolysis), the slight variations from proportionality involving a threshold intensity indicate that the reciprocity law does not hold exactly for the erythema reaction.

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[30] Stoll, B., *Helv. Phys. Acta*, **8**, 3 (1935); Locher, G. L., *Phys. Rev.*, **42**, 525 (1932); Audubert, R., and Reithmuller, C., *Compt. rend.*, **200**, 389 (1935); Karev, M., and Rodionov, S., *Z. Physik*, **92**, 615 (1934); Audubert, R., and Mattler, J., *Compt. rend.*, **206**, 1005 (1938).

[31] Eidinow, A., *Lancet*, **209**, No. 5320 (1925).

[32] Dorcas, M. J., and Forbes, G. S., *J. Am. Chem. Soc.*, **49**, 3081 (1927).

[33] Hausser, K. W., and Vahle, W., *Strahlentherapie*, **13** (1923); see Chapter 36.

There had been many attempts to devise methods of chemical actinometry, usually with the object of measuring the value of a source for producing erythema, but rarely had the physical principles underlying the method been analyzed with such thoroughness. Filters were rarely applied (or were used only in a relatively crude manner) and reliance was placed instead upon the choice of a reaction which might be effected within the same wave-length range as that of the reaction to be studied, if, indeed, any consideration at all was given to the matter. The absorption curve of the actinometer was usually taken as an index to the wave-length region within which it is photochemically effected. Variations in the efficiency of the monochromatic rays within the absorbed band were disregarded, and the possibility of the occurrence of side reactions were not always eliminated.

Kistiakowsky and Heidt[34] point out that, although the errors of radiometric measurements can be estimated only by the original investigator, many difficulties may be avoided by the proper use of actinometry, and that, if later, the given actinometer is restandardized, it is easy to recalculate all quantum yields previously referred to it. They describe in detail an apparatus whereby the quantum yield of a photochemical gas reaction over any time interval during its course may be stated in terms of the quantum yield of uranyl oxalate decomposed by monochromatic light of the same wave-length with a probable error of 5 per cent.

Gillam and Morton,[35] among the earlier writers on actinometry, proposed the photochemical reduction of potassium nitrate to nitrite (determined colorimetrically) as an index of the bactericidal activity of a source. The absorption of light by nitrates commences at 3300A, rises to a maximum at 3000A, falls to a minimum at 2650 and rises very rapidly beyond this point. The quantum efficiencies below 2860A are, however, much greater than those in the region of selective absorption, so that despite the dissimilarity in absorption of potassium nitrate and bacteria, the photolysis in solutions buffered to pH 9.4 was held to resemble the bactericidal reaction in respect to the spectral distribution of photochemical efficiency.

By this method Gillam and Morton found that an unused mercury lamp gave nitrite equal to 6.4 cc. of N/5000 nitrite, while a used mercury lamp gave only 1.6 cc. An iron-nickel arc produced 5.2 cc. in one hour at 6 inches, or 1.3 cc. at 12 inches, so that the old mercury lamp and the metal arc were effective to roughly the same extent. A test showed that about 98 per cent of the nitrite formed by exposure to the unfiltered lamp owed its origin to rays on the short-wave side of the limiting ray (2750A) transmitted by 0.090 inch of a Vitaglass filter. This was held to indicate that the unfiltered reaction is applicable for measuring the relative bactericidal efficiency of different light sources. The unfiltered reaction is also suitable for indicating the deterioriation of a quartz lamp since this deterioration begins in the short-wave region to which the nitrate photolysis is sensitive. The reaction is, however, too slow for general use as a routine test for dosage in actinotherapy. It has been employed by Kestner[36] in comparing various ultraviolet sources.

Webster, Hill and Eidinow[37] found the bleaching of a solution of methylene-blue in aqueous acetone to provide some guide to dosage in actinotherapy. The decomposition products of the acetone effect a bleaching of the dye which is proportional to the time of exposure, the dye evidently acting as a hydrogen acceptor.

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[34] Kistiakowsky, G. B., and Heidt, L. J., *J. Am Chem. Soc.*, **54,** 3246 (1932).

[35] Gillam, A. E., and Morton, R. A., *J. Soc. Chem. Ind*, **46,** 417 (1927); see Chapter 20 for further discussion of the reaction.

[36] Kestner, O., *Strahlentherapie*, **46,** 574 (1933).

[37] Webster, T., Hill, L., and Eidinow, A., *Lancet*, **1924,** (1) 745.

Gillam and Morton [38] found by the use of filters that about 88 per cent of the acetone-methylene blue reaction is due to rays between 2000 and 2800A, 6 per cent to rays between 2800 and 3250A, and 6 per cent to rays on the long-wave side of 3250A. This indicates that the test is unsuitable as a criterion for the exposures required to effect the conversion of sterols to vitamin D (Chapter 39). On the other hand, it might serve as a simple means of determining dosages in bactericidal experiments. Moss and Knapp[39] criticized the test as lacking delicacy.

With mercury-vapor lamps at short distances the acetone-methylene blue test is fairly rapid. It is rather slow in sunlight, but for recording the ultraviolet intensity over a whole day this is an advantage. Exclusion of air is essential for securing reproducible results by this method.[40]

The uranium-sensitized decomposition of oxalic acid was employed by Freer and Gibbs [41] in studying solar radiation in the tropics and was applied to the determination of the intensities of the radiations from the mercury vapor arc by Mathews and Dewey.[42] The test was standardized for actinometry by Anderson and Robinson,[43] Leighton and Forbes,[44] and by Forbes, Kistiakowsky and Heidt.[45]

The spectrum of an oxalic acid-uranyl salt solution exhibits considerable absorption in the region between 3000 and 3800A. In agreement with this were the experiments of Gillam and Morton with filters of Vitaglass and window glass and a mercury arc, which indicated that 25-30 per cent of the decomposition of the oxalic acid-uranyl salt is due to rays on the long-wave side of 3250A and about 40 per cent to rays longer than 2800A. The region 2700 to 3250A appeared to account for about 20 per cent of the change. With the change induced by sunlight taken as 100, that through 0.09 inch of Vitaglass was 86.7, and through 0.105 inch window glass, 67.5. The test appears to indicate in a very rough way the intensity of those radiations effective in producing erythema. Moss and Knapp [46] thought the test to be a measure of the rather indefinite dye fading power of a lamp. 4 mm. of Pyrex transmits 40 per cent, 8.2 mm. of clear Corex 70 per cent and red purple Corex (10.2 mm.), 19 per cent of the total radiation as measured by this method.[47] Erythema on the upper arm is said to be produced by the same quantity of radiation which decomposes 0.056 mg. of oxalic acid per square centimeter in three minutes under standard conditions.

The "Uroxameter" of Moss and Knapp [48] is an elaboration of this test, using a specially designed vessel (made by Baird and Tatlock) rotated during irradiation of thirty minutes at a distance of 6.5 inches. The test solution consisted of a mixture of 20 cc. of a 2-per cent aqueous solution of oxalic acid, 5 cc. of a 1-per cent solution of uranyl acetate in water, and 20 cc. of distilled water. For use with carbon arcs, an alternative stock solution richer in uranyl salt was recommended, and called the "20-strength" solution, since with it the distance of irradiation had to be greatly increased. The 20-strength solution was rather unstable, and had, according to Gillam and Morton, a somewhat different absorption spectrum than the normal mixture. Use of the stronger solution increases somewhat the values obtained through Vitaglass from a given source, the K.B.B. lamp. It was reported that a thickness of 2.2 mm. of the reacting solution absorbs all rays shorter than 3210A [49] and the method was said to indicate sensitivity to the region 3200-2300A. Brackett and Forbes [50] determined the gross quantum yields (see Chapter 12) at 21°C. (expressed as moles of oxalic acid per quantum) in a solution in which uranyl sulfate is 0.01 and oxalic acid 0.05 molar. The yields are 0.48 ± 0.01 at 2080A, 0.63 ± 0.03 at 2530A, and 0.59 ± 0.01 at 2780A. Forbes and Heidt [51] used uranyl oxalate rather than sulfate (.005 mole) and oxalic acid (.0025 mole) per liter. According to Pitzer, Gordon and Wilson [52] the rate of reduction of uranyl ion is small until just enough oxalic acid remains to form uranyl oxalate, when the rate of reduction rapidly increases. The presence of sulfuric acid has no effect on the relative rates. The photolyte in the actinometer is a complex, $H_2C_2O_4 \cdot UO_2C_2O_4$ which ionizes as a strong dibasic acid.

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[38] Gillam, A. E, and Morton, R. A., *J. Soc. Chem. Ind.*, **46**, 417 (1927).

[39] Moss, J. E., and Knapp, A. W., *J. Soc. Chem. Ind.*, **44**, 453 (1925).

[40] Osborn, T. W. B., and Stammers, A. D., *Brit. J. Actinotherapy*, **5**, 68 (1930).

[41] Freer, P. C., and Gibbs, H. D., *J. Phys. Chem.*, **16**, 709 (1912).

[42] Mathews, J. H., and Dewey, L. H., *J. Phys. Chem.*, **17**, 211 (1913).

[43] Anderson, W. T., Jr., and Robinson, F. W., *J. Am. Chem. Soc.*, **47**, 718 (1925).

[44] Leighton, P. A., and Forbes, G. S., *J. Am. Chem. Soc.*, **52**, 3139 (1930). In this paper the limitations of actinometry in polychromatic light are discussed.

[45] Forbes, G. S., Kistiakowsky, G. B., and Heidt, L. J., *J. Am. Chem. Soc.*, **54**, 3246 (1932). For a discussion of the reaction, see Chapter 24.

[46] Moss, J. E., and Knapp, A. W., *J. Soc. Chem. Ind.*, **44**, 453T (1925).

[47] Atkins, W. R. G., and Poole, H., *Sci. Proc. Roy. Dublin Soc.*, **19**, 355 (1929); *Brit. Chem. Abs.*, **A**, 1249 (1929).

[48] Moss, J. E., and Knapp, A. W., *J. Soc. Chem. Ind.*, **44**, 453T (1925); *Brit. J. Actinotherapy* (Jan., 1927).

The hydrolysis of monochloracetic acid has also been employed in actinometry.[53] Bagnall [54] reports that the amount of iodine liberated from a solution of potassium iodide acidified with sulfuric acid is a measure of the chemical activity of sunlight and Rousseau [55] used this reaction in testing the permeability of various substances to the ultraviolet. Moss and Knapp [56] suggested that the reaction should be carried out in quartz vessels. They also pointed out that unless one unit of ultraviolet radiation liberates the same quantity of iodine from the nearly colorless potassium iodide solution as from the orange-colored mixture of solutions of iodine and potassium iodide, the quantity of iodine liberated will not be directly proportional to the amount of ultraviolet radiation incident upon the solution. Hymas [57] finds that for periods less than ten minutes, the amount of reaction is proportional to the energy absorbed. The potassium iodide-starch method has a temperature coefficient between 25° and 62°C. of -1.042 for ten degrees. He also finds the deterioration of a mercury lamp to be apparently greater when tested by its action upon potassium iodide than by its action upon sensitized oxalic acid.

From their studies of various methods, Gillam and Morton concluded that the nitrate and carbon tetrachloride methods are most suited to measure the bactericidal rays, while the three oxalic acid methods are more suitable for measuring the "middle ultraviolet."

Clark [58] employs the rate of darkening of zinc sulfide as a measure of ultraviolet intensity. Zinc sulfide and lithopone are sensitive from about 2500A to about 3600A, with a maximum darkening at about 3200A. Mayerson[59] finds the method satisfactory if the change in reflection factor is measured. For measuring solar ultraviolet radiation, he finds the acetone-methylene blue the least applicable and the oxalic acid-uranyl sulfate reaction the most useful of these three methods. He presents a comparison of the data obtained by other workers with these methods, recalculated to absolute units.

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[49] Moss, J. E., and Knapp, A. W., *Brit. J. Actinotherapy*, May, 1927.

[50] Brackett, F. P., Jr., and Forbes, G. S., *J. Am. Chem. Soc.*, **55**, 4459 (1933).

[51] Forbes, G. S., and Heidt, L. J., *J. Am. Chem. Soc.*, **56**, 2363 (1934).

[52] Pitzer, E. C., Gordon, N. E., and Wilson, D. A., *J. Am. Chem. Soc.*, **58**, 67 (1936).

[53] Dain, B., and Puzenkin, E., *Ber. Ukrain. wiss. Forsch. physikal Chem.*, 4, 75 (1935); *Brit. Chem. Abs.*, **A**, 1211 (1935); *Chem. Abs.*, **29**, 2451 (1935).

[54] Bagnall, H. H., *Analyst*, **54**, 101 (1929).

[55] Rousseau, E., *Compt. rend. soc. biol.*, **93**, 1480, 1482 (1925).

[56] Moss, J. E., and Knapp, A. W., *Analyst*, **54**, 334 (1929).

[57] Hymas, F. C., *Quart. J. Pharm.*, **2**, 281 (1929).

[58] Clark, J., *Am. J. Physiol.*, **69**, 900 (1924); *Am. J. Hygiene*, **9**, 646 (1929); *J. Opt. Soc. Am.*, **21**, 240 (1931).

Eisenschimmel[60] suggested the diminution of the active chlorine content of chloramine-T in 0.2*N* solution in methanol as a measure of the intensity of actinic light. The reaction was carried out in glass test tubes. No information as to the effective wave-lengths is available.

Weyde and Frankenburger[61] measure the erythema-producing region of the ultraviolet by the photochemical formation of crystal violet in an alcoholic solution of its leucocyanide or sulfite. For radiations of 3130A and 2537A, the quantum efficiency is one. A small quantity of potassium cyanide or sulfite is added to the alcohol solution. By using sufficiently thick layers of solution, it is possible to measure 10^{15} dye molecules, corresponding to 6.8×10^{3} ergs. For ultra violet intensities of one erg per square centimeter, the exposure is one hour. Harris and Kaminsky[62] report that photolysis of crystal violet leucocyanide or sulfite is less desirable than photolysis of methylene-green leucocyanide for which the Einstein equivalence law (Chapter 12) holds with an accuracy of 2.5 per cent in absolute value and an average precision of 1.4 per cent for three wave-lengths. The latter reaction is said to be especially adapted for the measurement of very small light energies.

Anderson and Bird[63] used a fluorescence photometer with different chemical substances to measure the relative intensities of monochromatic ultraviolet light throughout the spectrum, and found that they could check the intensities as given by a thermopile. It was concluded that the photometric method may be employed for measuring accurately the ultraviolet energy.[64] Although fluorometers are simple and inexpensive,[65] Forbes[66] does not regard them as very precise.

Athanasiu[67] investigated the effects of light on voltaic cells. The latter were described as electrochemical actinometers. The maximum sensitivity of actinometers having electrodes of mercury salts in contact with 10 per cent sulfuric acid is at 2536A for mercurous chloride and at 2967 for mercurous bromide. The chloride and bromide are sensitive only to the ultraviolet; they are fluorescent under the latter, emitting a strong visible radiation. The effects were too great to be photoelectric and were attributed to photochemical changes at the surfaces of electrode-producing films. There are, in addition to an electrolyte, two similar metallic electrodes, one kept dark and the other irradiated. Polarization and thermal effects also play a part. With copper electrodes in copper sulfate, an

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[59] Mayerson, H. S., *Am. J. Hyg.*, **22**, 106 (1935).

[60] Eisenschimmel, W, *Z. Zuckerind. Cechoslov. Rep.*, **51**, 535 (1927), *Chem. Abs*, **22**, 356 (1928). The rate of combination of hydrogen and chlorine has been proposed as a measure of light intensity by C. Chilowsky, British P. 463,994, April 9, 1937, and 469,636, July 29, 1937; *Chem. Abs.*, **32**, 429 (1938).

[61] Weyde, E., and Frankenburger, W., *Trans. Faraday Soc.*, **27**, 561 (1932); U. S. P. 1,845,835, Feb. 16, 1932, of Frankenburger, W., Robl, R., and Zimmermann W.; *Naturwiss.*, **18**, 206 (1930); *Chem. Abs.*, **26**, 2121 (1932). Diazo compounds have also been employed in actinometers. N. V Chemische Fabrik, L. van der Grinten, French P. 820,108, Nov. 4, 1937; *Chem. Abs.*, **32**, 5307 (1938).

[62] Harris, L., and Kaminsky, J, *J. Am. Chem. Soc.*, **57**, 1154 (1935).

[63] Anderson, W. T., Jr., and Bird, L. F., *Phys. Rev.*, **32**, 293 (1928).

[64] See also Croad, A K., British P. 320,794 (1928).

[65] Winther, C., *Z. Elektrochem.*, **19**, 390 (1913); Gyemant, A., *J. Opt. Soc. Am*, **12**, 65 (1926).

[66] Forbes, G. S., *J. Phys. Chem*, **32**, 488 (1928).

[67] Athanasiu, G., *Compt. rend.*, **180**, 587 (1925); *J. Soc. Chem. Ind.*, 689A (1922); *Ann. Physique*, **4**, 318 (1925).

E.M.F. of the order of 40 millivolts can be obtained, the irradiated electrode being negative.[68]

Intensities of Various Lines as Related to Their Origins. The physical techniques described above have been applied to studies of the intensities of various lines and the results interpreted in terms of the probabilities of the occurrences of the corresponding transitions between energy states. These will not be discussed since the photochemist is more concerned with the broader features of the energy distribution of the spectral intensities within the various wave-lengths regions than with the physical theory of the intensities of individual lines.

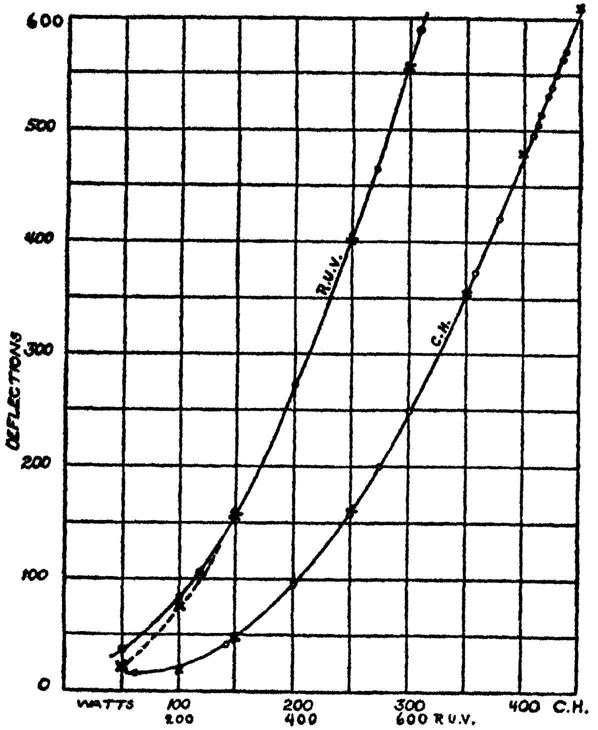

Figure 45. Variation in Total Radiation Emitted with Variation in Power Input (Coblentz, Long and Kahler, *Bureau of Standards Scientific Papers*).

Data on the Output and Spectral Distribution of Quartz Mercury Arcs

Hulburt[69] found the total radiation from 6000 to 2300A from a quartz mercury lamp as measured with a thermocouple to be 1.54×10^8 ergs per second. This would be equivalent to about 50 quanta emitted per mercury atom per second were all the energy at 5000A. Küch and Retschinsky[70] studied the spectral distribution of the energy from mercury arcs. They determined the total visible intensity and the intensities of individual visible lines by a flicker photometer, the ultraviolet by a photoelectric cell, and the continuous background by a photographic method. They also investigated absorption by mercury within the lamp.[71] Other early determinations of the energy distribution of this source were made by Ladenburg,[72] Hallwachs,[73] Fabry and Buisson,[74] Winther,[75] Allmand,[76] Souder,[77] Coblentz, Long and Kahler,[78] and Coblentz and Kahler.[79]

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[68] See also Iimori, S., and Takebe, T., *Sci. Papers, Inst. Phys. Chem. Research, Tokyo,* **8**, 131 (1928).

[69] Hulburt, E. O., *Phys. Rev.,* **31**, 1109 (1928); **32**, 593 (1928).

[70] Küch, R., and Retschinsky, T., *Ann. Physik,* **20**, 563 (1906); **22**, 595 (1907); see also Pflüger. *Ibid.,* **26**, 789 (1908); Athanasiu, G., *Compt. rend.,* **178**, 2071 (1924); Shoda, M., *Japan. J. Physics,* **9**, 27 (1934); *Chem. Abs.,* **28**, 4310 (1934); Koch, B., *Ann. Physik,* **33**, 335 (1939).

Coblentz, Long and Kahler give the variation of energy of wave-lengths less than 1.4μ as affected by variations in power input for a Cooper-Hewitt and an R.U.V. lamp. (Figure 45.) The experimental curves are closely represented by the formula $E = KW^x$, where for one lamp $K = 0.00462$ and $x = 1.83$ and for the other $K = 0.000457$ and $x = 2.314$.

Reeve[80] pointed out that the early work could not be used for a calculation of the absolute amount of energy emitted at any particular wave-length. He gave an intensity wave-length diagram for a 100-hour old Cooper-Hewitt 110-volt lamp operated at 62 volts and 4.2 amperes. In his diagram each "line" was given a triangular form, the base of the triangle being the wave-length region included. This method was adopted since the monochromator slit employed transmitted a finite range of wave-lengths rather than just the line width. Reflection and absorption losses, and the influence of compound lines, were considered.[81] For the relative energies of the mercury lines expressed in arbitrary units, he found the values given in Table 2.

Table 2.—Relative Energy of Mercury Lines.

Wave-length	Intensity	Wave-length	Intensity
248.5 mμ	7.1	303 mμ	82.5
254	39.5	313.5	213.0
265.5	35.1	334	9.4
270	6.6	366.5	326.0
275	2.3	406.5	111.4
280.5	20.3	437.5	166.6
290	17.9	559.	189.0
297	32.7	585.	207.

The early works contained some discrepancies in the ratios of the intensities of various lines. For example, Pflüger found that of the yellow line to the green line to be 140 to 90, while Ladenburg gave it as 27.4 to 42.9. The source of this and other discrepancies was attributed by Reeve to the influence upon the relative intensities of various lines of the electrical conditions, dimensions and age of the lamp.

A standard type commercial lamp run on 2.2 amperes and 10 volts per centimeter will deliver at an exit slit 40 × 1 mm. of a monochromator with 50 mm. objectives and an aperture ratio 4.5, 8×10^8 ergs per second at 3660A and 4×10^2 ergs per second at 2800A, where the energy of a quantum is nearly a third greater.[82]

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[71] Küch, R., and Retschinsky, T., *Ann. Physik,* **22,** 852 (1907).

[72] Ladenburg, E., *Physik. Z.,* **5,** 525 (1904).

[73] Hallwachs, W., *Ann. Physik,* **30,** 593 (1909).

[74] Fabry, C., and Buisson, H., *Compt. rend.,* **153,** 93 (1911).

[75] Winther, C., *Z Elektrochem.,* **20,** 109 (1914).

[76] Allmand, A. J., *J. Chem. Soc. Trans.,* **107,** 682 (1915).

[77] Souder, W. H., *Phys. Rev.,* **8,** 316 (1916).

[78] Coblentz, W. W., Long, M. B., and Kahler, H., *Bur. Standards Sci. Paper,* No. 330 (1918).

[79] Coblentz, W. W., and Kahler, H., *Ibid.* No. 378, 233 (1920).

[79] Coblentz, W. W., and Kahler, H., *Ibid.* No. 378, 233 (1920); see also Boll, M., *Compt. rend.,* **156,** 313 (1913); *J. Chem. Soc.,* **104,** 182 (1913).

[80] Reeve, L., *J. Phys. Chem.,* **29,** 39 (1925).

[81] Franklin, R., Maddison, R., and Reeve, L., *Ibid.,* **29,** 713 (1925).

Beesley and Ridyard[83] recorded the energy distribution of a Uviol lamp burning at 29.5 volts and 2.42 amperes, and compared it with the data previously obtained by Allmand,[84] as well as with the energy distribution of the quartz mercury lamp. Their data are not included here as this lamp is now rarely used in photochemical work.

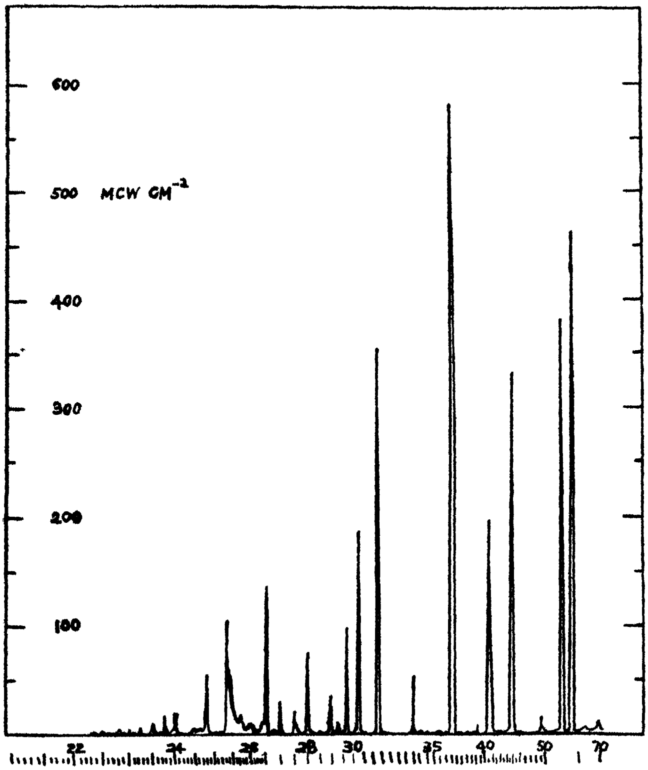

FIGURE 46. (McAlister, *Smithsonian Miscellaneous Collections.*)

Atkins and Poole[85] compared photochemical and photoelectric measurements of the radiation from a mercury vapor lamp. Andant and Lecompte[86] recorded the relative intensities of the principal lines from the yellow doublet to 2536A emitted by mercury vapor lamps of various designs functioning under different conditions. For the same arc, the intensity of emitted radiation changes greatly with the arrangement of the apparatus, especially with the voltage at the terminals. For two different arcs and for the same spectral line, an identical variation in each lamp does not produce the same effect on the emission.

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[82] Forbes, G. S., and Harrison, G. R., *J. Am. Chem. Soc.*, **47**, 2449 (1925).
[83] Beesley, E., and Ridyard, H. N., *J. Phys. Chem.*, **32**, 1342 (1928).
[84] Allmand, A. J., *J. Chem. Soc.*, **107**, 682 (1915).
[85] Atkins, W. R. G., and Poole, H. H., *Sci. Proc. Roy. Dublin Soc.*, **19**, 355 (1929).
[86] Andant, A., and Lecompte, J., *J. Phys. Radium*, **1**, 65 (1930).

The relative intensities of prominent lines in the ultraviolet have been studied by Coblentz, Stair and Hague.[87] Absolute intensities in the visible and ultraviolet ranges have been recorded by McAlister.[88] In Figure 46 are given the intensities of 32 lines at 250 mm. from a 20 mm. midsection of a 400-hour-old Cooper-Hewitt direct current arc operated at high intensity (4.5 amperes and 150 volts). These values, expressed in microwatts per square centimeter may be multiplied by 7.1 to obtain approximate values for the full length of the arc exposed. Figure 47 gives similar data for the same arc operated at low intensity (3.0 amperes and 44 volts).

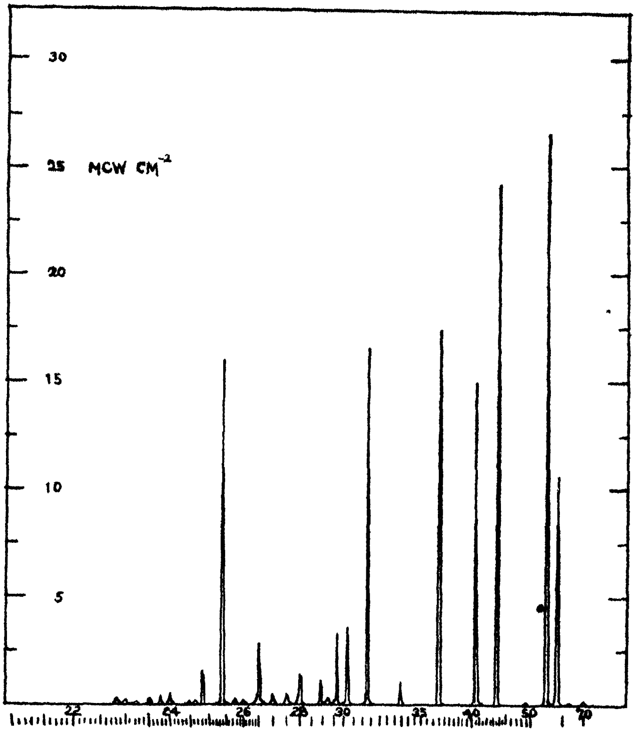

FIGURE 47. (McAlister, *Smithsonian Miscellaneous Collections.*)

In the former case the vapor pressure of the mercury is approximately atmospheric; in the latter it is but a few millimeters. Microphotometer curves of spectrograms in the region of the resonance line (Figure 48) show that even under low intensity conditions, the resonance line is partly reversed by absorption by mercury vapor, and that at high intensity conditions it is completely absorbed.[89] The mercury arc usually employed apparently does not emit this resonance line. In the high intensity arc, the energy in this region is all due to the neighboring 2534.8A line and to the continuous background. Four different arcs showed differences averaging 5 per cent for some lines, the maximum being 10 per cent for the 2537A line.

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[87] Coblentz, W. W., Stair, R., and Hague, J. M., *Bur. Standards J. Research*, **8**, 760 (1932).

[88] McAlister, E. D., *Smithsonian Miscellaneous Collections*, **87**, No. 17 (1933).

[89] Wood, R. W., [*Phil. Mag.*, **23**, 689 (1912)] found mercury vapor to absorb its resonance line so strongly that a quartz bulb filled with mercury vapor at room temperature (vapor pressure 0.001 mm.) casts a shadow when illuminated by this line alone. A thickness of 0.5 mm. reduces the intensity to one-third its initial value. This is not the only line absorbed by mercury vapor under arc conditions. Crew, W. H., and Dawson, L. H., [*J. Opt. Soc. Am.*, **17**, 261 (1928)] found some thirteen lines, including two "spark lines" to show self-reversal. For further studies, see Hughes, A., and Thomas, A., *Phys. Rev.*, **30**, 466 (1927); Mohler, F. L., and Moore, H. R., *J. Opt. Soc. Am.*, **15**, 74 (1927); Kopfermann, H., and Tietze, W., *Z. Physik*, **56**, 604 (1929).

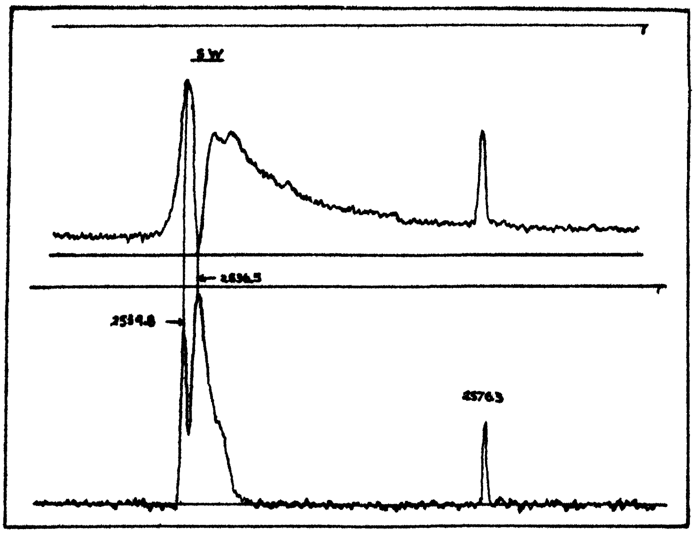

Figure 48. Microphotometer Curves in the Region of the Resonance Line (From McAlister, *Smithsonian Miscellaneous Collections*).

Observations made with the aid of filters (Table 3) showed the distribution of energy into various regions.

Table 3.—Distribution of Energy for Mercury Arcs.

		1 0.2-0.35μ	2 .35-1 4μ	3 1.4-19μ	4 >19μ	5 Total
High Intensity.						
20 mm. of vertical arc	mcw. cm.$^{-2}$	84	167	245	68	564
	per cent	14.8	29.7	43.4	12.1	100
Total vertical arc	mcw. cm.$^{-2}$	600	1130	2710	350	4700
	per cent	12.5	23.6	56.6	7.3	100
Total horizontal arc	mcw. cm.$^{-2}$	615	995	2700	370	4680
	per cent	13.2	21.2	57.7	7.9	100
Low Intensity.						
20 mm. of vertical arc	per cent	3.0	8.0	81.7	8.3	100
	mcw. cm.$^{-2}$	2.8	7.7	77.5	8.0	96
Total vertical arc	mcw. cm.$^{-2}$	19.8	59.6	704.8	124.	908.
	per cent	2.3	6.6	77.6	13.5	100.

Forsythe, Barnes and Easley[90] have compared the intensities, distribution, and output of ultraviolet radiation from the quartz mercury arc and several types of

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[90] Forsythe, W. E., Barnes, B. T., and Easley, M. A., *J. Opt. Soc. Am.*, **21**, 30 (1931); **24**, 178 (1934).

"sun lamp" (see Chapter 8), and Waguet[91] has studied the light emission of mercury arcs at high pressure. Other relative data, obtained with a spectrometer and thermopile with galvanometer, were given by Oguri.[92]

It has been shown[93] that the spectrum of the light from a given mercury arc varies in character and intensity with the part of the lamp from which the light is emitted. The variation occurs because of irregularities in the thickness and curvature of the quartz envelope. For accurate spectrographic work, this source of error may be remedied by inserting a plane quartz window in the side of the burner.

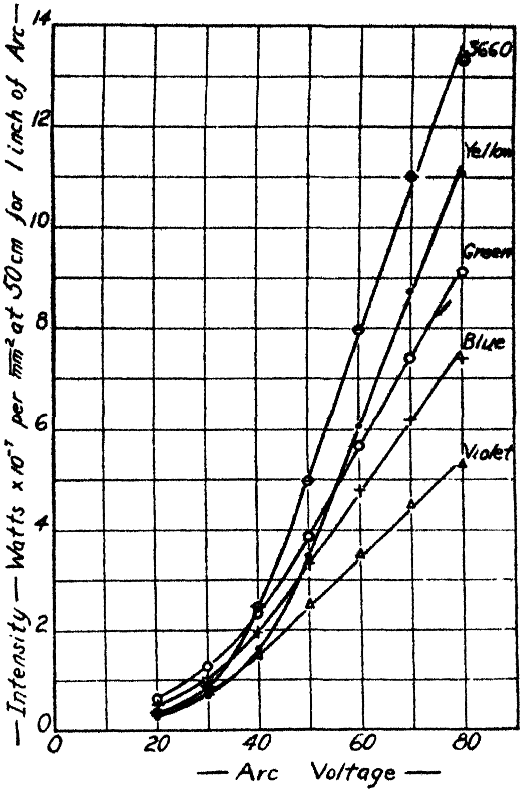

FIGURE 49.

Effect of Arc Voltage on Intensities of Line Groups (Johnson and Burns, *Journal Optical Society of America*).

Absolute line intensity and energy distribution data in high and low-pressure arcs were obtained by Johnson and Burns,[94] employing a method of photographic photometry (using as comparison a standardized mercury arc) developed by Stockbarger and Johnson. In this method, characteristic curves for the plates were taken for each line measured. Variations of the line intensity with current or voltage were measured on a quartz radiometer, and converted into absolute units by comparison with the absolute values determined by photographic photometry at one current and voltage.

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[91] Waguet, P., *Compt. rend.*, **201**, 450 (1935). See also Kern, J., *Z. tech. Physic*, **19**, 249 (1938); *Chem. Abs.*, **32**, 8929 (1938), and Larché, K., and Rössler, F., *Physik. Z.*, **37**, 800 (1936); *Chem. Abs.*, **31**, 6549 (1937).

[92] Oguri, S., *J. Chem. Ind. (Japan)*, **38**, Suppl. binding, 392 (1935); **39**, 35, 143 (1936); *Brit. Chem. Abs.*, **B**, 635 (1936).

[93] Takahashi, T., and Clark, L. H., *J. Sci. Instruments*, **6**, 273 (1929).

[94] Johnson, L. B., and Burns, L., *J. Opt. Soc. Am.*, **23**, 55 (1933).

The vertical type high-pressure arc had an arc length of three inches. The current was kept at 4 amperes by a hand-controlled rheostat and the voltage was maintained at 45 volts by a voltmeter, photoelectric cell and an amplifier so arranged as

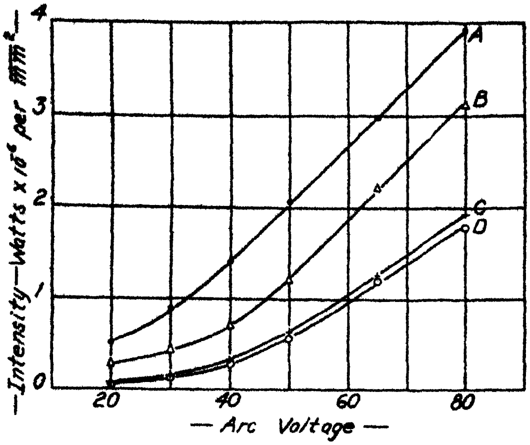

FIGURE 50.

Effect of Arc Voltage on Output in Four Spectral Regions (Johnson and Burns, *Journal Optical Society of America*).

to control the voltage through the temperature by regulating a blast of air on the cathode of the arc. Table 4 gives the intensities of the visible and near ultraviolet lines. The low pressure arc was 22 inches long and was operated at 4 amperes and approximately 37 volts.

Table 4.—Intensities of Visible and Near-Ultraviolet Lines.

Group	Line	Intensity (watts × 10^{-6}/mm^2 at 50 cm. for 1 inch of arc) High-pressure arc	Low-pressure arc
Yellow	5791A	0.102	0.009
	5770	0.124	0.010
Green	5461	0.305	0.057
Blue	4358	0.232	0.053
	4348	0.014	0.0008
	4339	0.006	0.0003
Violet	4078	0.022	0.0058
	4047	0.170	0.042
3660	3663	0.075	0.0068
	3655	0.086	0.0075
	3650	0.190	0.0126

Figure 49 shows the variation of the intensities of the line groups with arc voltage for the high-pressure arc carrying 4 amperes. The results confirm the data of earlier workers that lines of the same series (5461, 4358 and 4047, which give most of the radiation in their groups) increase in intensity together and retain their intensity ratios.

By the use of filters, the total radiation was divided into four regions (A, 14,000-40,000A; B, 3800-14,000A; C, 2950-3800A; D, 1850-2950A) and the varia-

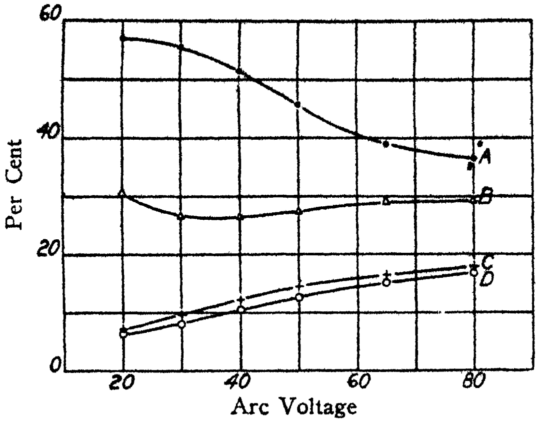

FIGURE 51.

Effect of Arc Voltage on Relative Output in Various Regions (Johnson and Burns, *Journal Optical Society of America*).

tions of the intensities of each with arc voltage are shown in Figure 50. The total radiation for the whole arc, including the electrodes, was determined in microwatts per square mm. at 50 cm. The variation of intensity with the voltage is shown in Table 5.

Table 5.—Variation of Intensity with Arc Voltage

Arc voltage	80	70	60	50	40	30	20
Intensity	10.74	8 60	6.50	4.43	2.72	1.57	0.888

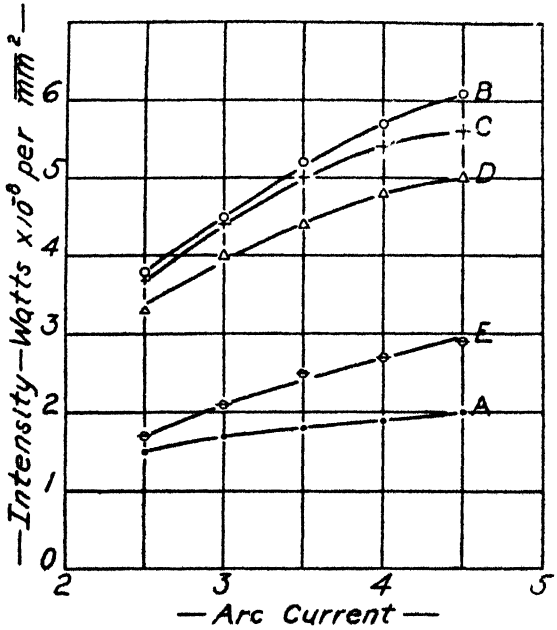

FIGURE 52.

Effect of Current on Intensities of Line Groups (Low-pressure Arc) (Johnson and Burns, *Journal Optical Society of America*).

In Figure 51, the results secured are expressed in terms of the variation of the per cent of the total radiation in each of these regions with arc voltage (at 4 amperes).

For the low-pressure arc, the variation of the intensity of the groups of lines of Table 4 with the current at 37 volts, is given in Figure 52. The low-pressure arc was very sensitive to drafts and changes in room temperature. Immediately after a sudden reduction in the arc current, the total intensity went up, but after ten or fifteen minutes came back to approximately the same value. If the arc was running at 40 volts and a blast of air was played upon it, the arc voltage would decrease until a minimum was reached at about 36 volts. At this point, if the arc was further cooled, the voltage would again increase. The line intensity depended on whether the arc was running on the hot or the cold side of the minimum. The data in the figures were obtained on the hot side.

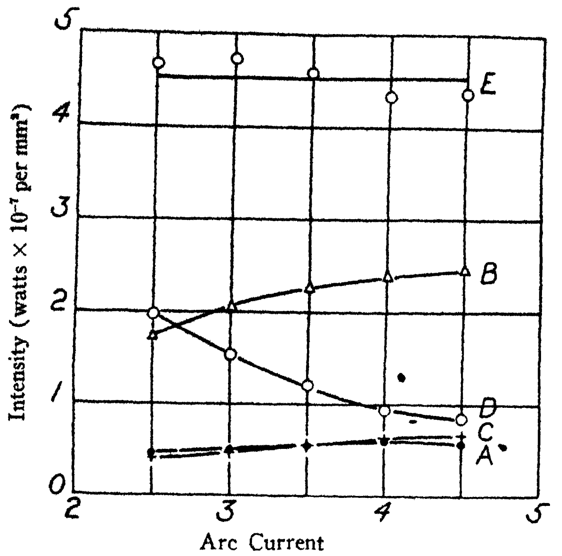

FIGURE 53.

Effect of Current on Output in Four Spectral Regions (Johnson and Burns, *Journal Optical Society of America*).

The variations with arc current of the intensities of each of the four regions separated by the filters from five inches of arc are given in Figure 53 along with the total intensity (curve E). The latter is believed to be constant, the variation of the individual points from a horizontal line being ascribed to the sensitivity of the arc to varying ventilation. The effect of variation of the arc current on the energy distribution is given in Table 6. It is important to note that at 2.5 amperes, the intensity of the far ultraviolet reaches the high value of 43.5 per cent, and it appears likely that at lower currents, still higher percentages may be found, although the arc then becomes very unstable unless there is accurate temperature control of the surrounding air. Johnson and Burns also included data for the low-pressure arc in Uviol glass, and in UV 690 and UV 888 glasses.

Table 6.—Energy Distribution for Various Arc Currents.

Region	4.5 amp.	4.0 amp.	3.5 amp.	3.0 amp.	2.5 amp.
14000-40000A	12.3%	13.0%	11.9%	11.0%	9.9%
3800-14000A	53.9	52.8	50.0	45.0	37.8
2950-3800A	15.0	13.4	12.0	10.3	8.8
1850-2950A	18.8	20.8	26.1	33.7	43.5

Owen and Wright[95] have considered the effects of the position of the arc upon the spectroscopic analysis of the ultraviolet. Data comparing energy-emission for various artificial sources of ultraviolet radiation have been reported by van Wijk and Reerink,[96] Greider[97] and by Krefft and Pirani,[98] the latter dealing chiefly with sources of infrared rays.

Forbes and Leighton[99] indicated the complex nature of the factors controlling the intensity of a given line and showed that for any line and current strength, the maximum intensity is proportional to the pressure, the slopes and intercepts varying with the wave-length and internal diameter of the lamp. This relation was true up to five atmospheres in the constricted arc, but in a 9-mm. arc at high pressures the intensity increases less rapidly than the pressure. The latter phenomenon was attributed to the presence of a 3-mm. shell of absorbing vapor.

Harrison and Forbes[100] found that for a given power input, the intensity is much greater for high voltages and pressure and low current than it is for high current and low voltage and pressure. In Table 7 are given for the wave-length regions arbitrarily numbered in column 1 (including the lines in column 2) a rough estimate of the relative intensities of the various components of each group. The measurements were obtained with a spectroradiometer with a silver-bismuth thermopile. No corrections were made for reflection or absorption in the optical train, or for the effective slit-width. Only the relative intensities of single lines were measured.

Table 7.—Relative Intensity of Various Wave-lengths.

Group	Wave-lengths	Relative Intensity	Group	Wave-length	Relative Intensity
1, 2	selective quartz radiation	?	9	3663	4
				3655	6
				3650	10
3	11288A	2			
	10140	5	10	3352	..
				3342	..
4.	6234	1			
	6152	2	11	3132	4
				3126	5
5	5819	3			
	5804	3	12	3026	1
	5790	3		3024	2
	5769	6		3022	2
	5461	5			
			13	2804	1
7	4539	5			
	4348	5	14	2700	2
8	4078	3	15	2537	2
	4047	3			
			16	2438, etc.	1

Also, it was pointed out that the intensity of any line increases linearly (at constant current maintained by varying the ventilation of the arc) as the voltage gradient is increased beyond a limiting value which varies with the individual line and the current. Table 8 shows for the numbered groups the ratio of the intensities to that of the yellow-green lines (maximum or group five) for various voltages at 2.5 amperes. The energy of the 3660 line was found to be increased 17.1 times by a 3.5-fold increase of the voltage gradient (from 4 to 14 volts per centimeter). Also it was stated that at 4.5 amperes and 25 watts per centimeter, only half as much energy will go into the yellow-green maximum as will when the current is 1.5 amperes and the voltage three times as great. For high efficiency, the arc should be cooled as little as possible. The ratio of intensities of any two lines of the same series was essentially constant.

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[95] Owen, E. A., and Wright, P., *Brit. J. Radiol.*, **5**, 330 (1932).

[96] van Wijk, A., and Reerink, E. H., *Physica*, **13**, 289 (1933).

[97] Greider, C. E., *Ind. Eng. Chem.*, **23**, 508 (1931).

[98] Krefft, H., and Pirani, M., *Z. tech. Physik*, **14**, 393 (1933).

[99] Forbes, G. S., and Leighton, P. A., *J. Opt. Soc. Am.*, **12**, 53 (1926)

[100] Harrison, G. R., and Forbes, G. S., *J. Opt. Soc. Am.*, **10**, 1 (1925).

Table 8.—Relative Intensity of Groups to Yellow-Green Line.

	Ratio to Maximum Five (Yellow-green Lines) at				
Maximum	5 Volts	7 Volts	9 Volts	11 Volts	14 Volts
3	0.347	0.337	0.359	0.375	0.402
5	1.000	....	....	....	....
7	0.725	0.738	0.655	0.600	0.562
8	0.375	0.474	0.407	0.369	0.345
9	0.909	1.100	1.120	1.080	1.050
10	0.587	0.705	0.638	0.545	0 545
12	0.173	0.279	0.303	0.332	0.329
14	0.013	0.147	0.168	0.166	0.165
15	0.013	0.170	0.180	0.171	0.165

The average arc shows the smallest change in energy distribution for a given variation in total intensity when the pressure is as high as possible. As this is the condition of greatest intensity of all the maxima, the best operating conditions seem to comprise as high a pressure and voltage drop as is consistent with the life of the lamp and with its mechanical structure.

Asada[101] proposes for the relation between the light intensity, the current and the potential difference, the expression, $G=kI(V-a)^n$, where G is the light intensity, k a constant, I the current, V the potential, a is a lamp constant determined as the least terminal voltage, and n is a constant for any given wave-length. The relation holds for both alternating-current and direct-current lamps, effective values being used in the former case. The value of n depends upon the type of current used.

Harris[102] found that there is a great outburst of ultraviolet energy from a cold lamp immediately after striking the arc, the current then having a maximal value and the resistance and voltage minimal values. This initial flare is quite evanescent, being followed by a sudden fall to the real onset of the permanent vaporizing and incandescent period. The latter begins after the first minute of arc striking has elapsed.[103] During the next two minutes, the voltage doubles and the lamp warms up, raising the vapor to incandescence. In the second and third minutes, a precipitous rise in emission occurs, the slope of which can be affected by controlling the temperature of the lamp. A blast of air causes the emission to rise slowly to its final value. A parabolic reflector behind the lamp reduces the rate of cooling on one side, so that incandescence is reached more quickly, but the emission falls again to a level slightly below that of the lamp under normal conditions in still air. For a constant source, the arc with a fan directed upon it, is to be chosen. Under these conditions, devitrification and discoloration of the quartz is reduced, avoiding the rapid fall in efficiency most marked in the extreme ultraviolet. Figure 54[104] shows in the left half the changes (on starting the Uviarc) which occur in the total energy, energy of the arc and electrodes, and arc alone, the latter only being concerned with the emission of the mercury lines. The right half of the figure shows in heavy lines the effect of cooling the arc on the increase of current, the energy expended in the arc, electrodes and arc and the total watts. In lighter lines are shown the corresponding effect of increasing the series resistance. Maddock[105] plotted arc watts—intensity variation curves for temperature variation of the air surrounding the burner, and tabulated absolute intensities for thirty lines between 7000 and 2300A.

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[101] Asada, T., *J. Elec. Eng. Inst. (Japan)*, **51**, 36 (1931); *Chem. Abs.*, **26**, 1522 (1932).

[102] Harris, D. T., *Rev. Sci. Instruments*, **6**, 2 (1929).

[103] See also Watters, B. D., *Brit. J. Radiology*, **81**, 163 (1924).

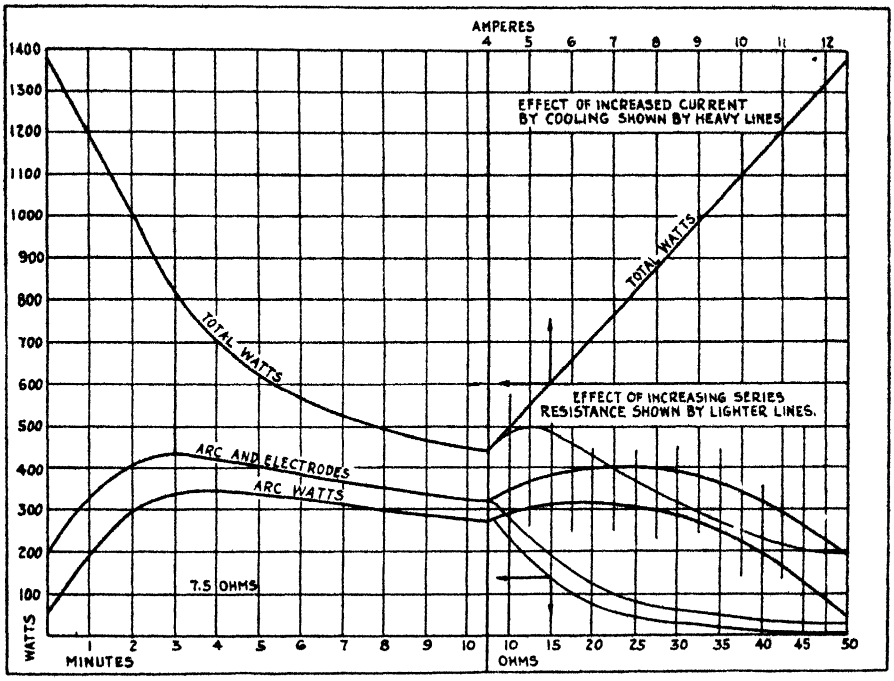

FIGURE 54. Energy Distribution under Various Operating Conditions (Buttolph, *Review Scientific Instruments*).

MEANS FOR INCREASING THE OUTPUT OF THE RESONANCE LINE

To issue from the lamp the light of the bright radiant axial thread must first penetrate the envelope of vapor and undergo absorption. To obviate this absorption effect the temperature of the envelope may be reduced thereby lowering the vapor pressure. This can be effected by cooling with water, but owing to condensation of mercury vapor, a coating of mercury may form on the inside wall of the lamp and prevent the issuance of light. Another method of preventing the limita-

[104] Buttolph, L. J., *Rev. Sci. Instruments*, 1, 497 (1930).

[105] Maddock, A. J., *Proc. Phys. Soc. (London)*, 47, 424 (1935).

tion of the output by absorption, used particularly in lamps for the study of resonance phenomena where a strong emission of the resonance line is required, is based upon[106] deflection of the arc toward one side of the tube of the lamp by means of an electromagnet. This operation is said to raise the temperature of the tube at the place where the arc is applied, thus burning an aperture in the film resulting from condensation. The light of the deflected radiating arc will issue through this aperture without having penetrated an absorbing layer of mercury vapor. Figure 55 shows the construction of this apparatus.

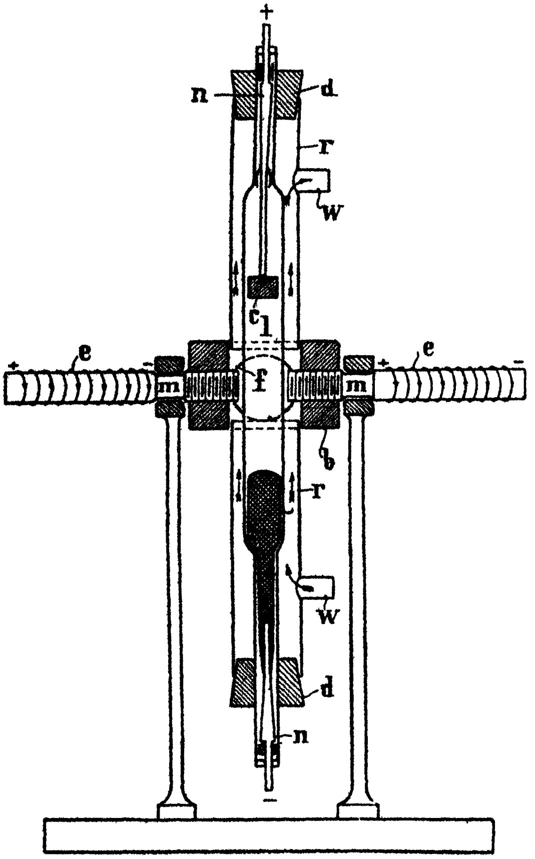

FIGURE 55.

Kerschbaum's Apparatus for Magnetic Deflection of the Mercury-vapor Arc.

The brass block (b) has a vertical bore; into this are soldered two tubes (r) having branches (w) for receiving and discharging the cooling water. Into this vertical cooler is inserted a quartz mercury-vapor lamp (1), which is fastened above and below by means of bored rubber stoppers (d). The quartz lamp is a vertically burning lamp, which is of the simplest and most compact construction possible. As leading-in members for the lamp, ground-in nickel-steel pins (n) serve. Only the metal of the lower electrode (cathode) is mercury. The anode is a piece of carbon (c) screwed on the end of the upper nickel-steel pin. The brass block (b) has in addition two lateral, horizontal, threaded bores. By means of these apertures the ends of two iron rods (m) are screwed up close to the wall of the lamp; over these rods are pushed coils of wire (e). Each of the two coils has 200 turns of covered copper wire of ½ ohm resistance; the current employed is 2 to 3 amperes. The electromagnets so formed produce lines of force at right angles to the axis of the lamp. The block (b) has another horizontal bore (f). This passes through only the rear half of the block and can be closed by a quartz plate. When the lamp is burning and the electromagnets are so connected that they deflect the arc to the rear, the light will issue through the bore (f) and enclosing quartz plate. The arc is drawn by rotating the lamp into its horizontal position. Tanberg [107] has studied the physical phenomena involved in the passage of a mercury arc at low vapor pressure in a magnetic field.

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[106] Kerschbaum, F., U. S. P. 1,118,868, November 24, 1914; *Chem. Abs.*, 8, 2315 (1914).

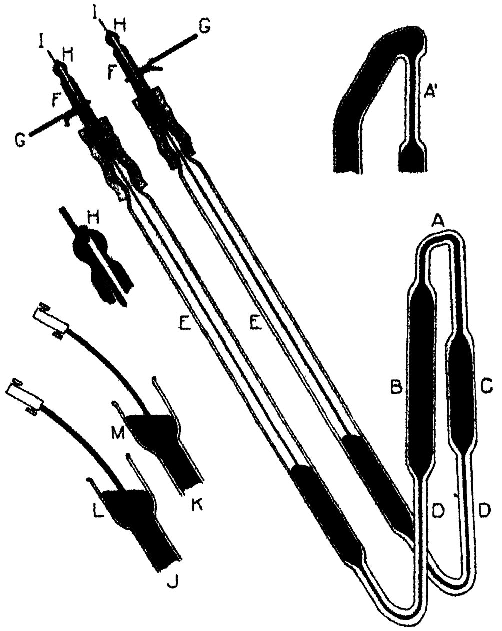

FIGURE 56. Diagram of the constricted arc, arranged for pressures up to five atmospheres and currents from 0.2 to 2.0 amperes. The inserts show at A′ the modified form of the constricted portion, arranged to water-cool the hot column so that currents up to 5.0 amperes could be used, and below the enlarged ends arranged for work at atmospheric pressure (Forbes and Harrison, *Journal of the Optical Society of America*).

The Constricted Arc. In these arcs the non-luminous portion of the arc is eliminated by making the tube of such narrow diameter that it is practically completely filled by the narrow luminous thread. They are usually laboratory made, and may be operated at pressures up to about 5 atmospheres, but are comparatively short-lived. Harrington [108] described a lamp operated on 25 volts direct current (10 volts per centimeter), yielding a brilliant light of capillary tube dimensions.[109] Vincent and Biggs [110] described an arc with a 0.3 mm. column, open to the air and carrying 0.1 to 0.16 ampere at 100-150 volts; it had low current capacity. Harrison and Forbes [111] designed two special lamps. The first of these (Figure 56) had in A a bent tube 63 mm. long, of 2.0 mm. bore and 7 mm. external diameter. It extended between two mercury reservoirs, one at a higher level than the other. The one at the higher level was made negative, so that it would not fall as the result of the transfer of mercury by the current. The tubes (B and C) of 5 mm. internal diameter joined the ends of the arc tube to capillaries DD of 0.5 mm. bore and 11 cm. long. Their purpose was to restrain oscillations but they were large enough to carry 5 amperes without undue heating. These were bent through 135°, and joined to parallel tubes, E,E, of 8 mm. bore and 20 cm. long, mounted on a grooved strip of wood. By supporting the lamp so that BAC sloped down and EF sloped upward, the latter could be boiled out in a few minutes through the capillaries and beyond by means of a Bunsen burner, no pump being needed. The open ends of the lamp led to short steel tubes FF soldered to leads GG of a 550-volt dynamo run by an induction motor. Arrangements were described also for operating the lamp under higher pressures obtained by means of a tire pump. At higher pressures this lamp was much more effective than arcs of greater section.

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[107] Tanberg, R., *Nature*, 124, 371 (1929). See also Fabrikant, V. A., and Rokhlin, G., *Compt. rend. acad. sci. U.R.S.S.*, 19, 393 (1938); *Chem. Abs.*, 32, 8256 (1938).

[108] Harrington, E. L., *J. Opt. Soc. Am.*, 7, 689 (1923).

In a modified form the constriction was made only 38 mm. long, the ends of the tubes were open to the atmosphere and enlargements L,M, retarded changes in level due to the transfer of mercury. By putting the ends of a long U trough under the end of L and above M, the mercury transferred to the cathode trickled down the trough to the anode and made the operation automatic. Three amperes were required; for currents greater than 2 amperes, the constriction must be water-cooled.

In Table 9 the effect of variations of voltage and current upon the pressure in and the intensity emitted by such a constricted arc between 3650 and 3663A are listed. A 15-fold variation was made in the current and in the voltage, but not in these simultaneously; the result was a 160-fold variation in pressure and a 400-fold variation in the intensity of the 3660 line. The authors gave graphically the intensity vs. voltage-gradient curves at one ampere for six different wave-length maxima, as well as at 0.33 ampere (12-58 volts per cm.) for pressures ranging from 0.1 to 5 atmospheres. The first arc constructed had a section of 50 square

Table 9.—Effect of Voltage and Current on Arcs.

Pressure, mm.	Volts per cm	Amperes	Watts per mm $^2 \times 10^{6}$
88	11.7	0.33	7.00
654	28.4	0.33	39.0
3920	57.6	0.33	268
29	7.4	1.00	15.0
208	13.8	1.00	43.0
664	21.4	1.00	137.
1398	28.2	1.00	392.
752	21.7	3.02	940
752	27.8	4.00	2090
752	29.5	5.00	2600

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[109] Harrington, E. L. See also *Phil. Mag.*, (7) 4, 836 (1927).

[110] Vincent, J. H., and Biggs, G. D., *J. Sci. Instruments*, 1, 242 (1924).

[111] Harrison, G. R., and Forbes, G. S., *J. Opt. Soc. Am.*, 11, 99 (1925); *J. Am Chem Soc.*, 47, 2449 (1925).

mm., a later one of about 3. The curves for the first showed a sharper bend and a straighter upper portion; those of the constricted arc showed a more uniform curvature. The curves for the larger arc bent and began to ascend steeply at about 6 volts per cm., but in those of the constricted arc this occurred at about 20 volts per cm. There was no evidence of a decrease in efficiency as the pressure increased up to five atmospheres.

The absorption of all lines, especially of 2537A, the shortest mercury arc line of sufficient intensity for general use in photochemical work, was diminished in the constricted arc. This line could be kept at constant intensity by tripling the current from 0.33 to 1.00 ampere, and cutting the voltage down from 62 to 32 volts per cm., thereby reducing the pressure from 4000 to 1500 mm. The greatest advantage of this type of arc seemed to lie in its high internal resistance, giving higher efficiencies at normal pressures, so that an increase in current becomes more nearly equivalent to an increase in voltage in the production of higher intensities. There was a tremendous relative increase in the 3663A line at high currents, while all the ultraviolet maxima except that at 2537A showed higher relative values at high currents.

For studying reactions with very low photochemical yields, there is required a source giving very great light intensities with at the same time a high degree of spectral resolution. These requirements were most nearly met by a portable constricted arc between two mercury surfaces, confined in a water-cooled quartz tube of 2 mm. internal, and 7-mm. external, diameter, 38 mm. long, with its ends open to the atmosphere. This lamp could be repaired easily and could be refilled and boiled out in ten minutes. There were no sealed-in leads to fail, no possibility of damage on reversing the polarity, and no tungsten electrode to sputter, the latter being a chief cause of the decrease in ultraviolet output of other arcs.[112] The constricted arc furnished (per square millimeter of exit slit of a monochromator) energy flux up to 30 times that available from a commercial lamp run at normal rating.

A further modification was designed by Leighton and Forbes[113] to combine as fully as possible the long life of large diameter arcs with the high intensity of the constricted arc. The legs of an inverted U of 6 mm. internal diameter dipped into mercury reservoirs left open to the atmosphere. A 5-mm. capillary, nearly filled with an iron wire, attached to each arm of the U rendered oscillation negligible. The electrodes were water-cooled, and by adjusting the relative heights of the water and electrode surfaces, mercury transfer was neutralized. The distribution of the energy flux (determined by the aid of a monochromator and thermopile) is given in Table 10.

Table 10—Distribution of Energy Flux.

A	10,140	5770	4350	4060	3660	3130	3020	2800	2700	2540
Ergs/sec. mm.^{2}	325	910	490	360	900	610	420	100	150	99

Crist[114] gave directions for making an arc that will run at 4 to 4.5 amperes and 20-25 volts per centimeter for over thirty hours with fairly constant intensity.

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[112] Fabry, C., and Buisson, H., *Compt. rend.*, **153**, 93 (1911).

[113] Leighton, P. A., and Forbes, G. S., *J. Am. Chem. Soc.*, **51**, 3550 (1929).

[114] Crist, R. H., *J. Am. Chem. Soc.*, **52**, 4337 (1930).

He later [115] put a transverse magnetic field across the arc to displace the latter to the back wall, thereby decreasing devitrification at the front wall. Other capillary mercury-vapor lamps have been described by Heidt and Daniels,[116] by Heidt and Forbes,[117] and by Hoffman and Daniels.[118] The model of Forbes and Heidt eliminated cemented joints and the objectionable capillaries used in the earlier lamps to check mercury oscillations. Quartz tubing of 8-mm. internal diameter was used. Figure 57 is an axonometric view of the device, which was about 30 cm. in height. One feature of the apparatus is the tapered "Pyrex" plungers P, ground into tapers in the quartz walls at J. After the lamp is filled, these plungers are lowered until oscillations of mercury are negligible, but the plungers are not lowered quite enough to close the joints completely; otherwise the lamp will melt or blow up. Tungsten wires W are sealed into the ends of the plungers, and when the latter are filled with mercury, a current path of negligible resistance, incapable of arcing, is provided. The two tubes U stand in open rectangular copper tanks (not shown), about 160 mm. (right) and 60 mm. (left) deep. Obviously, the length of either side of the arc (in one case, 150 mm. from M to M_1) can be changed by varying

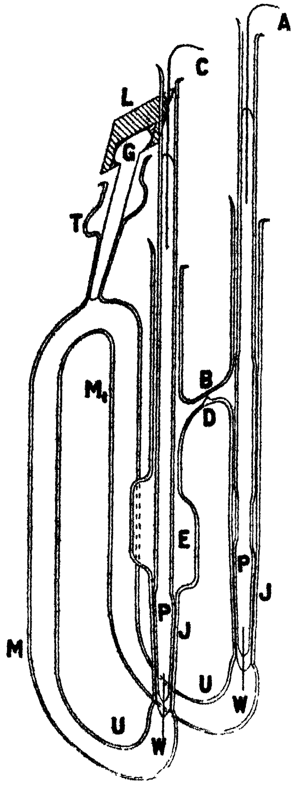

FIGURE 57.

Quartz Mercury-vapor Lamp of Forbes and Heidt (*Journal American Chemical Society*).

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[115] Crist, R. H., *J. Am. Chem. Soc.*, 54, 3939 (1932).
[116] Heidt, L. J., and Daniels, F., *J. Am. Chem. Soc.*, 52, 2151 (1930); 54, 2381 (1932).
[117] Heidt, L. J., and Forbes, G. S., *J. Am. Chem. Soc.*, 53, 4349 (1931).
[118] Hoffman, R. M., and Daniels, F., *J. Am. Chem. Soc.*, 54, 4226 (1932).

the depth of the corresponding tank. Tubes soldered in, top and bottom, permit rapid circulation of water.

The lamp is filled and boiled out through the tap T, provided with a ground-in quartz plug G held down by the lead weight L and sealed with mercury. The tap is bent 30° from the vertical, to prevent hot air ascending during operation from distilling the mercury out of the lamp. After closing the circuit through a suitable resistance, the arc is started by holding a flame below T. This arc sinks to the water surfaces, and operates at 3.5 amperes and 170 volts. As a much larger amount of mercury is displaced on the cathode side, the enlargement at E is necessary to accommodate it. As the mercury distils from the hot cathode to the cooler anode, it returns by the bridge B, which has a dam D to break up the trickles into drops and thus avoids momentary short circuits. With a steady source of current, and nearly constant barometric pressure and ventilation, the total variation in light intensity over considerable periods seldom exceeds 3 per cent.[119]

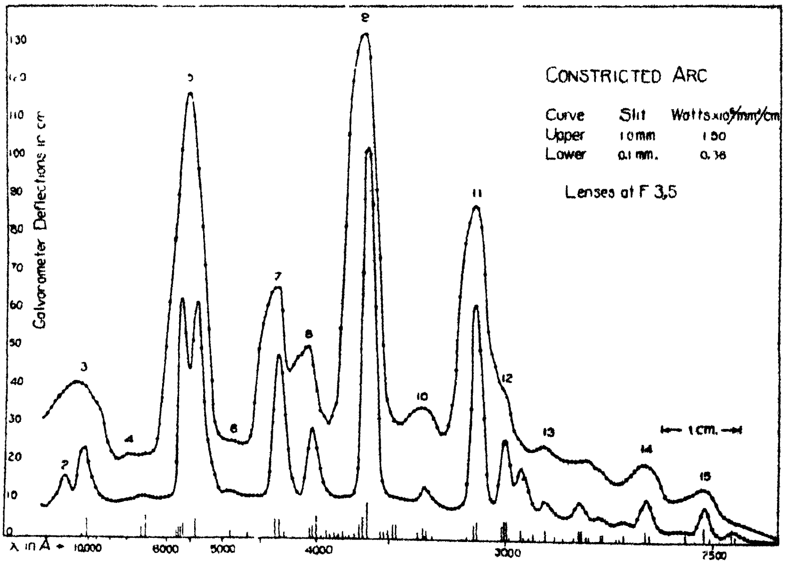

FIGURE 58. Spectral Energy Distribution Curves for the Constricted Arc (Forbes and Harrison, *Journal American Chemical Society*).

Forbes and Harrison[120] presented a wave-length vs. energy curve (Figure 58) for a constricted arc in a water-cooled quartz tube of 2 mm. internal and 7 mm. external diameter, 38 mm. long with its ends open to the air and running on 3 amperes and 90 volts. A monochromator was used as a spectroradiometer. The lower curve, showing greater resolution, was obtained with an entrance slit of 0.1 mm., and the upper one with 1 mm. In the latter case, 140 ohms resistance was in series with the galvanometer and thermopile so that 1.0 cm. deflection corresponded to 1.50 microwatts per square millimeter at the exit slit. In the lower curve, 0.36 microwatt was the corresponding figure. Along the wave-length axis are short, vertical lines indicating the number and approximate relative intensities (in a given group) of the various lines making up each maximum, as determined from a spectrogram of the light from the arc taken with an instrument of higher resolving power; the weaker lines are all relatively fainter than indicated. At the highest intensities used with the constricted arc, 490 microwatts per square millimeter of approximately monochromatic light of 3660A were issuing from a monochromator slit 1 × 40 mm. or a total energy flux of about 196,000 ergs per second. Elenbaas [121] has described a water-cooled constricted arc which operates under mercury pressures of 5 to 25 atmospheres.

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[119] For a simple magnetic method of starting this lamp, see Wilson, L. D., *J. Am. Chem. Soc.*, 58, 856 (1936).

[120] Forbes, G. S., and Harrison, G. R., *J. Am. Chem. Soc.*, 47, 2449 (1925).

In working with laboratory-made lamps, caution must be taken to avoid mercury poisoning. Attention was directed to the insidious onset of mercury poisoning and to the difficulty of cure by Stock,[122] who described details of hygienic measures which should be taken in laboratories where work with mercury is conducted. Stock asserted that 0.01 or 0.001 mg. daily produces disturbances of the health. His warning excited considerable comment,[123] much, but by no means all of which, was confirmatory. The importance of the matter makes thorough toxicological studies highly desirable. Aside from the question of toxicity, there is a recorded instance of the explosion of a quartz mercury lamp, filling the laboratory with dangerous vapors and igniting nearby flammable materials.[124]

A discussion of the impurities of mercury and the methods recommended for purification of the latter has been given by Booth and Jones,[125] who also describe in detail an unbreakable still capable of distilling three to five kg. of mercury per hour.

Water-Cooled Arcs. It is possible to lessen the absorption of the resonance radiation within the lamp by converting the latter into a low pressure arc by immersing the cathode in water. This procedure is not recommended in the case of commercial arcs. This caution does not, however, apply to those arcs, chiefly sold for therapeutic applications, which are designed for water-cooled operation. The arc is in this case operated with practically the same high voltage, high pressure and medium current density natural for air cooled arcs.

A design of a mercury-vapor lamp yielding nearly "cold light" is described by Billon-Daguerre, Medard and Fontaine.[126] The lamp is in the form of an inverted U-tube and is made of fused silica. Electrodes of Invar enter the ends of the tube. A short intense arc is formed at the bend of the tube between the columns of mercury on either side. The lamp is enclosed in a transparent silica flask (the wall of which is paraboloidal and silvered to act as a reflector) and is immersed in a tank of water. The light is concentrated by the mirror and emerges through a silica window in the tank. The lamp consumes 18 amperes, either alternating or direct current at 70 volts, and yields 3000 candlepower. The light can be used for microscopy and projection work without heating the specimens or celluloid films. The mercury lamp is said to possess an advantage over the carbon arc in that the luminous point remains fixed and requires no regulation. Application of such lamps to water sterilization and submarine photography has been suggested.

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[121] Elenbaas, W., *Rev. optique*, **15**, 343 (1936). See also Harada, T., and Azuma, T., *Proc. Phys.-Math. Soc. Japan*, **19**, 677 (1937); *Chem. Abs.*, **31**, 8365 (1937); Egyesult Izzolampa és Villamossagi R. T., British P. 482,070, March 23, 1938; *Chem. Abs*, **32**, 6562 (1938), Bol, C., *Phys. Rev.*, **52**, 214 (1937).

[122] Stock, A., *Z. angew. Chem*, **39**, 461, 984 (1926); **41**, 663 (1928); *Biochem. Z.*, **216**, 243 (1929).

[123] Schmidy, A., *Z. angew. Chem.*, **39**, 786 (1926); Pincus, G., *Ibid.*, 787; Reihlan, H., *Ibid.*, 788; Wolf, L., *Ibid.*, 789; Ruska, J., *Ibid.*, 790 (1926); Hoffmann, F. G., *Chem. Ztg.*, **50**, 927 (1926); Holtzmann, *Z. angew. Chem*, **40**, 438 (1927); Winderlich, R., *Chem Ztg.*, **52**, 629 (1928); Kröner, W., *Chem. Ztg.*, **52**, 121 (1928); Podrouzek, R. N. V., *Chem. Listy*, **22**, 529 (1929).

[124] Mechlin, F. J., *Ind Eng. Chem.*, **19**, 859 (1927).

[125] Booth, H. S., and Jones, N. C., *Ind. Eng. Chem.*, **19**, 104 (1927).

[126] Billon-Daguerre, A. L., Medard, L., and Fontaine, H., *Compt. rend.*, **157**, 921 (1914).

Bates and Taylor[127] developed a cooled arc of C702P "Pyrex" glass with tungsten leads. Through the center were two concentric quartz tubes, R_1 and R_2 (Figure 59). R_1 is the reaction vessel for photochemical changes while R_2 is a water-jacket to prevent R_1 from becoming overheated by the action of the arcs. Outside, the glass system was sealed to quartz by rubber tape and by Gooch crucible tubing, wired and shellacked to permit operation of the arc at 100°C. The seals were protected by coils of lead pipe D carrying cold water. N is the negative electrode and A,B,C_1 and C_2 are all positive. N and A are tungsten leads covered by just enough mercury to cause the two surfaces to come together on jarring. An arc is formed which jumps to B, a nickel cone welded to tungsten.

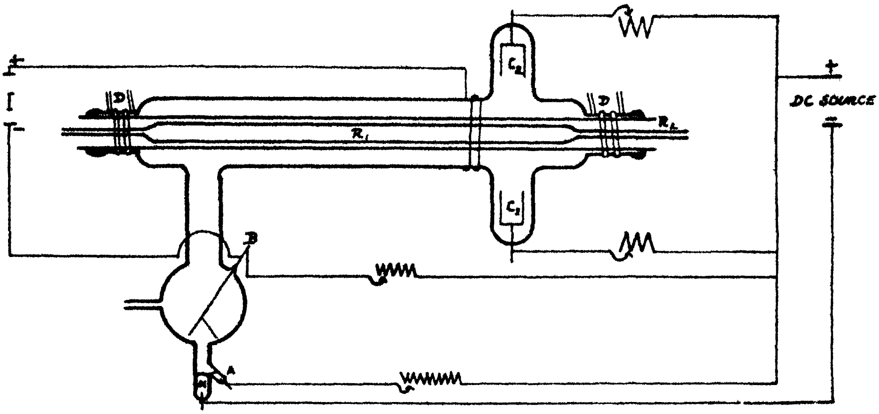

FIGURE 59. Mercury Arc for Study of Mercury-Sensitized Photochemical Reactions (Bates and Taylor, *Journal American Chemical Society*).

This serves as an electrode and also deflects mercury vapor from N against the walls of the bulb, kept in a water bath. This regulates the vapor pressure in the arc to that of mercury at the bath temperature. The arc can be brought up to the electrodes C_1 and C_2 by breaking down the space charge by an induction coil, the secondary of which is shown at I. C_1 and C_2 are two cylindrical nickel electrodes. The potential necessary depends to a large extent on the geometry of the arc. R_2 is 2.5 cm. in diameter and 45 cm. long, R_1 1.5 cm. by 37 cm., the surrounding glass arc being 40 cm. by 5 cm. The side tubes containing C_1 and C_2 are 3.5 cm. in diameter and 5 cm. long. The side tube with bulb and mercury reservoir is 30 cm. long and 3.5 cm. in diameter, while the diameter of the bulb is 6 cm. This has a drop of 35 volts from C_1 and C_2 to N when running at 18 amperes. The slide-wire resistances are of such size and capacity that the current from A to N is 0.5 ampere, B to N, 5 amperes, and from C_1 to C_2 to N up to 10 amperes each. C_1 and C_2 must have separate resistances or the current would flow entirely to one of them, giving an unevenly distributed discharge. After the arc has been started, B may be disconnected, but A should remain in the circuit to insure a steady arc. Due to leaks around the seals, the arc can be run only with a mercury pump in continual operation. If the arc is run with air in too large quantity, not only do the electrodes become oxidized, causing the arc to emit a pink glow, but the mercury tends to wet the glass between A and N making it impossible to start the arc. When the arc is first set up or after a long period of disuse, the nickel electrodes must be degassed by the passage of a current greater than that ordinarily used. The temperature of the water in R_2 should be kept above that of the bulb to prevent distillation of mercury from N, which would cut down the light.

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[127] Bates, J. R., and Taylor, H. S., *J. Am. Chem. Soc.*, 49, 2438 (1927).

A water-cooled lamp of the mercury anode type is in extensive use for medical work. The cooling serves to protect the tissues from the heat of the arc, so that it is possible to secure a high intensity of ultraviolet, particularly in the short-wave region, by reducing the distance between the source and the area treated. The lamp has a U-shaped quartz tube, *A*, the bend of which is in a plane perpendicular to the plane of the arms. (Figure 60.) The tube carries on the ends two mercury containers *BB* at right angles to the plane of the arc tube, and these constitute the electrode vessels to which the current is conducted by ground-in mercury-sealed rods *CC*. The arc is formed in the portion of the tube which is surrounded by a jacket of quartz, so shaped as to maintain an approximately equal distance between the walls of the tube and the envelope, to make the cooling uniform. The space is filled with a suitable gas, the thermal conductivity of which affects the electrical characteristics of the arc.[128] Between this jacket and the outer housing of the apparatus, water is circulated. The light is emitted through a quartz window in front of the casing, after passing through a layer of water. The compact form made possible by this construction, known as the Kromayer,[129] is advantageous for many purposes. A form with a double anode for alternating current operation also has been prepared.

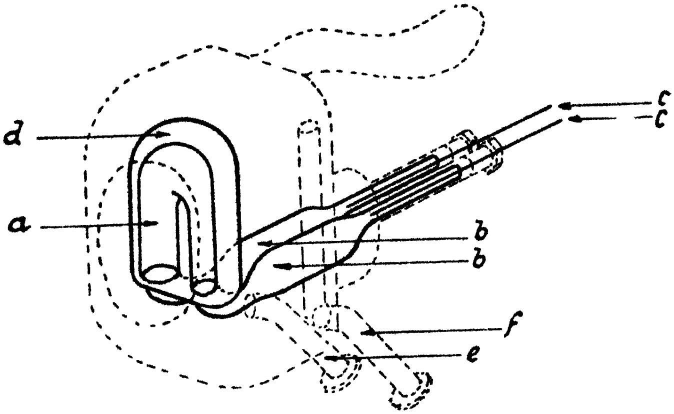

FIGURE 60. Kromayer Lamp.

Other manufacturers, notably the Burdick Corporation, employ the Uviarc as the source for a water-cooled lamp. The infrared rays are removed by a sealed quartz filter cell containing pure water. The cell is incompletely filled to permit expansion of the water as the lamp heats up. A stream of flowing water surrounds the filter cell and serves to cool it. This stream of water does not come into contact with any quartz surface through which the rays must pass, eliminating any loss of transparency due to the deposition of solids. An air-space between the filter-cell and the quartz face of the lamp further eliminates heat by conduction. See Figure 61. An automatic shutoff to protect the lamp when the water flow fails has been described by Piatti.[180] Another liquid-cooled lamp for photochemical work is due to Goltstein.[181]

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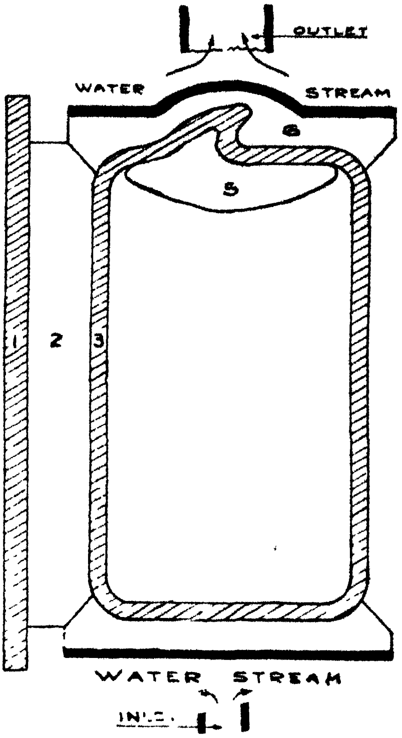
[128] Anderson, W. T., Jr., U. S. P. 1,749,994, March 11, 1930 (to Hanovia Co.); British P. 296,527, Sept. 6, 1928; French P. 638,802, Aug. 3, 1927; British P. 356,056, Sept. 3, 1931.

[129] Hanovia Chemical and Manufacturing Co.



Courtesy Burdick Corporation.

FIGURE 61.

Ever-Clear Window of Burdick Water-cooled Lamp. Cross Section: Side View. 1. Quartz outer face. 2. Air space to eliminate heat by conduction. 3. Fused quartz window. 4. Lens of distilled water to filter out infrared. 5. Evacuated space to allow for expansion of water. 6. Soft-metal case to protect the quartz window.

THE DETERIORATION OF QUARTZ MERCURY ARCS

Deterioration of the lamps was a serious problem to the earlier manufacturers of mercury arcs. The literature is filled with many observations of lamp failure. Poorly constructed lamps caused some of these.[182] Others were inaccurate because of the use of unsatisfactory actinometric methods for measuring the output.

In early lamps, Coblentz found that the percentage of the total radiation shorter than 4500A decreases from an initial value of 70 per cent to about 50 per cent after 1000 to 5000 hours. This included the strong groups of lines at 4360 and 4060A.

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[180] Piatti, L., *Physik. Z.*, **31**, 182 (1930).

[181] Goltstein, E., U. S. P. 1,669,819, May 15, 1928; *Chem. Abs.*, **22**, 2296 (1928). For a recent inexpensive source of mercury resonance radiation of high intensity, see Steacie, E. W. R., and Phillips, N. W. F., *Can. J. Research*, **16B**, 220 (1938).

[182] See, *e.g.*, Bordier, H., *Arch. Elec. Med.*, **1910**, 396; Courmont, J., and Nogier, T., *Compt. rend.*, **152**, 1746 (1911); *Illuminating Engineer*, London, **4**, 503 (1911); Le Bon, G., *Compt rend.*, **153**, 49 (1911); Moss, J. E., and Knapp, A. W., *J. Soc. Chem. Ind.*, **44**, 453 (1925).

The total output decreased to about one-half to one-third of its initial value.[183] Thermopile observations showed no marked difference in the proportion of ultraviolet emitted during the first 500 hours of use. The data of Table 11 represent the output as measured in galvanometer scale deflections.

Table 11.—Effect of Age upon Radiation.

Age in hours	0	97	177	343	450	522	640	783	959	1064	1140
Total radiation below 14,000A	1611	1497	1503	1380	1033	910	1104	1107	1069	1025	1034
Ultraviolet less than 4500A as % of total	69.4	67.8	60.4	...	59.9	58.2	54.8	52.3	50.8	...	49.1

Nelson[184] found that a burner (Curve A, Figure 62) which had been used for 500 hours had lost none of its effectiveness in testing ageing on paints. Another burner, B, was first used for 1600 hours, at which time its effectiveness had decreased markedly. The deposit on the surface of the quartz was then removed as far as possible by heating the quartz with a blast burner and the lamp again used for 250 hours. The relative intensities of the two burners A and B in the region shorter than 3100A were found to be in the ratio of 1.7 to 1 when used at 220-240 volts and 6.5 amperes, indicating a decrease of about 40 per cent for the old burner.

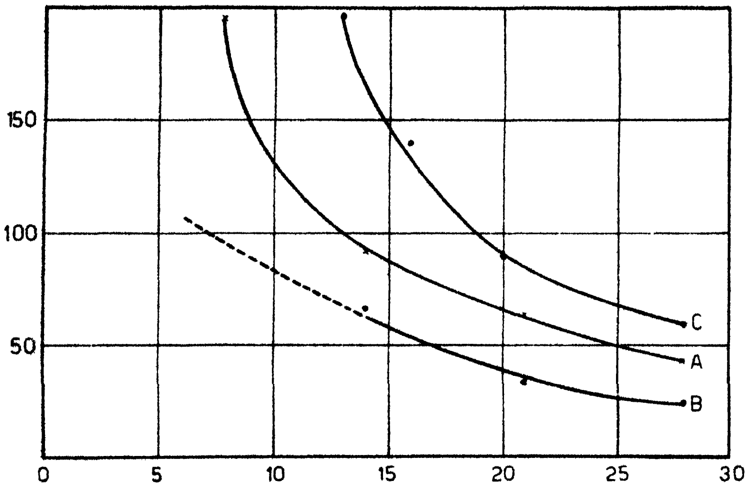

FIGURE 62. (Nelson, *Proceedings American Society for Testing Materials.*)

Reeve[185] found by physical methods that 500 hours of use caused a decline in the intensity of a commercial lamp at 2540A of 60 per cent and of the 3660A lines of 28 per cent. Thus, the decrease is most marked in the extreme ultraviolet. It was believed that for arcs employed in quantitative work in the region 2480 to 2890A, the energy distribution should be determined every 200 hours. The energy in this region was thought to be considerably reduced during the first 500 hours. The 2485A line sometimes disappeared within 100 hours and the 2300, 2340, 2370 and 2400A lines were ineffective after less than 50 hours. Similar observations were recorded by Gillam and Morton,[136] who believed that after a rapid fall in the output of the extreme ultraviolet in the first 150 to 200 hours, the output becomes fairly constant. After this first change, there occurs a slow nonselective loss in transmission of the burner. The first effect was thought due to the formation of SiO vapor inside the lamp and the second to the gradual deposition of a film of opaque silicon.

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[183] Coblentz, W. W., Long, M., and Kahler, H., *J. Frank. Inst.*, **187**, 112 (1919); *Bureau of Standards Sci. Papers*, 330 (1918). Note also *Sci. Papers* 378 and 495.

[184] Nelson, H. A., *Proc. Am. Soc. Testing Materials*, **22**, II, 485 (1923).

[185] Reeve, L., *J. Phys. Chem.*, **29**, 39 (1925); Cunliffe, P. W., Franklin, R., Maddison, R., and Reeve, L., *Ibid.*, **30**, 1427 (1926).

Hanovia lamps (Luxor B Alpine Sunlamp) are said to drop to 80 per cent of their initial emission in the first 300 hours, after which they remain fairly constant showing 73 per cent after 2000 hours.

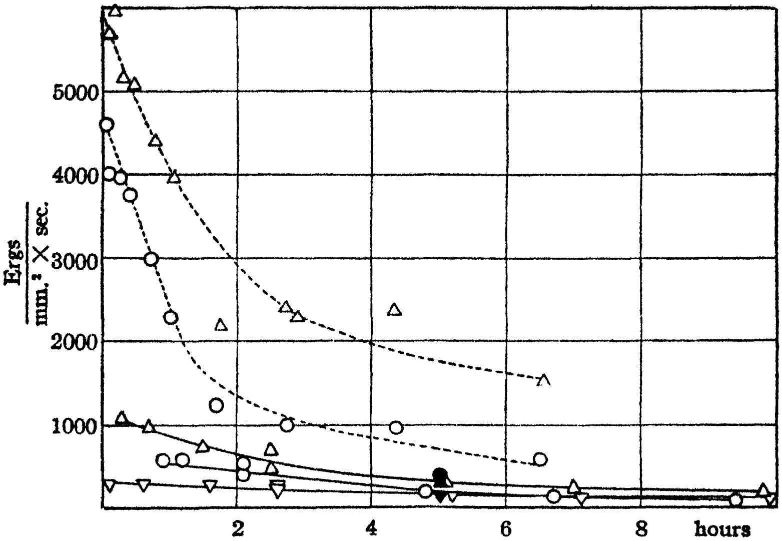

FIGURE 63. Rate of Deterioration of Constricted Lamp (Forbes and Harrison, *Journal American Chemical Society*).

Flynn[137] suggested that for a 220-volt lamp, an increase in the voltage at the rate of two volts per 100 hours of operation would compensate for the ageing loss.

Kolbert[138] proposed a circuit with variable resistance coil or tapped transformer and control switch marked on the dial so as to operate a lamp at 140, 150, 155, 160, 165 and 170 volts after 100, 250, 400, 600, 800 and 1000 hours, respectively. The manufacturers of the Uviarc recommended that during the first 500 hours the voltage be increased 3 per cent each 100 hours.

Devitrification in quartz plays only a secondary role in ageing, according to Meyn.[139] There is a black deposit on the inner surface, a part of which can be rubbed off or removed by acids. Another deposit penetrated to a depth of 0.1 mm. and was thought to be either finely-divided mercury or elemental silicon. Buttolph has published a photomicrograph taken by Dr. Hodge of the Stevens Institute[140] of the inner surface of a glass tube of a mercury arc. The surface was densely and uniformly pitted. This probably occurs also in quartz tubes, increases with increased temperature, voltage or any other factor that increases bombardment by electrons or by mercury molecules or ions. In burners with tungsten anodes, sputtering of these has long been recognized as a factor in ageing. Figure 63 shows the rate of decline in energy per sq. mm. of exit slit of the constricted arc for three wave-lengths.[141] Inverted triangles indicate 4060A, upright triangles 3660 and circles 2540A. Dotted lines give the output of the constricted arc on 94 volts and 4.9 amperes, solid lines on 78 volts and 2.1 amperes. All intensities were multiplied by ten. The three blacked-in points indicate a new commercial arc on 82 volts and 4.1 amperes. A new constriction was inserted before the run with 2.1 amperes and this was cleaned and revitrified before that with 4.9 amperes. The deterioration of the constricted arc is rapid, being 50 per cent for the first hour at 2540A and 5 amperes. This rate falls off greatly with increase in time and wave-length and with decrease in current.

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[136] Gillam, A. E., and Morton, R. A., *Phil. Mag.*, 6, 1123 (1928).

[137] Flynn, O. R., *Am. Dyestuff Reptr.*, 12, 837 (1923).

[138] Kolbert, J. W., British P. 413,921, July 26, 1934, to British Hanovia Co., Ltd.

[139] Meyn, W., *Z. wiss. Phot.*, 25, 345 (1927); *Brit. Chem. Abs.*, 677, B (1928).

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[140] Buttolph, L. J., *Trans. Electrochem. Soc.*, **65**, 148 (1934).
[141] Forbes, G. S., and Harrison, G. R., *J. Am. Chem Soc*, **47**, 2453 (1925).

Chapter 8

Mercury Discharge Lamps

Since the radiations from a mercury lamp are emitted from mercury vapor in the positive column, it is evident that, if mercury vapor is made to fill the lamp by vaporization from any reservoir, a mercury cathode is not essential. George[1] devised a lamp in which tungsten electrodes were used and the mercury was vaporized from a separate spherical bulb connected with the quartz tube by a narrow-bore tube. Before the lamp had heated up sufficiently to vaporize the mercury, the discharge was carried by an inert gas under pressure. George[2] stated that the ultraviolet output might be increased by using alternating current at high voltage and frequency. The terminals were connected with the inductance of an oscillating circuit, although other ways of converting local alternating current to a high frequency were also suggested.

The use of tungsten cathodes as a source for the emission of electrons at high voltages was limited by their tendency to sputter and blacken the lamp envelope. Greater progress was based upon the discovery by Wehnelt[3] that calcium oxide fused onto the surface of heated platinum forms a cathode of high electron emissivity at lower temperatures than are necessary for tungsten. Such cathodes were employed in the construction of lamps by Konen and Jungjohann.[4] According to Buttolph,[5] in more recent developments, nickel has replaced platinum as the base. Much work has also been done upon the development of cathodes in which alkaline-earth oxides with various additions have been applied to spirals of wire.[6] The theory of the operation of this type of cathode, and particularly, of the manner in which the physical or chemical union of the coating and base material affects satisfactory operation, lies beyond the scope of this book.[7]

The oxide-coated type of cathode can also be made with such elements as sodium and caesium.[8] The choice of metal and activating coating depends on the operating temperature, vapor pressure and other features of the design. In some cases, the oxide-coated cathodes are brought to the necessary cathode temperature directly by the cathode voltage drop and arc current. This is the arrangement in the low-voltage Cooper-Hewitt mercury rectifier lamp and in the high intensity mercury arc of the General Electric Vapor Lamp Co. In some cases, they receive a preliminary heating by a glow discharge facilitated by a starting gas. Because of the rather limited heat available for starting and for operation, the lamps are made as small and of as low a heat radiating and heat capacity as possible. In other lamps, the cathodes are separately heated by special elements. A number of cathodes have been described by Buttolph.[9]

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[1] George H., U. S. P. 1,361,710 (1920); *J. Soc. Chem. Ind.*, **40,** 75A (1921).

[2] George, H., U. S. P. 1,671,109, May 29, 1928; British P. 234,834, March 18, 1926.

[3] Wehnelt, A., *Ann. Physik,* **14,** 425 (1904).

[4] Konen, H., and Jungjohann, W., *Verhandl. deutsch. Physik. Ges.*, **3,** 145 (1910).

[5] Buttolph, L. J., *Trans. Illum. Eng. Soc.*, **28,** 153 (1933); **30,** 151 (1935).

[6] Spanner, H. J., and Doering, U. W., British P. 397,162, Aug. 8, 1933; Meyer, F., and Spanner, H. J., British P. 274,027, Oct. 20, 1927; Germer, E., French P. 707,198, April 13, 1931; Anderson, W. T., Jr., and Fraser, H. D., U. S. P. 1,890,926, Dec. 13, 1932; British P. 394,367 and 394,388; Spanner, H. J., Doering, U. W., and Germer, E., German P. 597,580, May 26, 1934.

[7] Dushman, S., *Rev. Modern Physics,* **2,** 381 (1930); Reimann, A. L., *Phil. Mag.*, **12,** 1073 (1931), Becker, J. A., *Phys. Rev.*, **34,** 1323 (1929); Druyvesteyn, M. J., and Warmoltz, N., *Physica,* **4,** 41 (1937); Suhrmann, R., and Frühling. G., *Naturwiss.*, **26,** 108 (1938).

[8] Becker, J. A., and Sears, W., *Phys. Rev.*, **38,** 2193 (1931); Benjamin, M., and Rooksby, H. P., *Phil. Mag.*, **15,** 810 (1933).

The gas or metal vapor conducting arcs may be designed for the utilization of the emission of the radiations from the positive column, as in tubular lamps, or of that of the negative glow as in certain lamps of bulbular form. It is not possible to give an account of the many varieties of these lamps which have been proposed. Since much of the development of these lamps as ultraviolet sources has been intimately associated with the development of lamps for visible lighting, an historical account would involve much extraneous material. It is interesting to note that the development of modern gaseous conduction lamps has been based in large part upon the pioneering work of McFarlan Moore.[10]

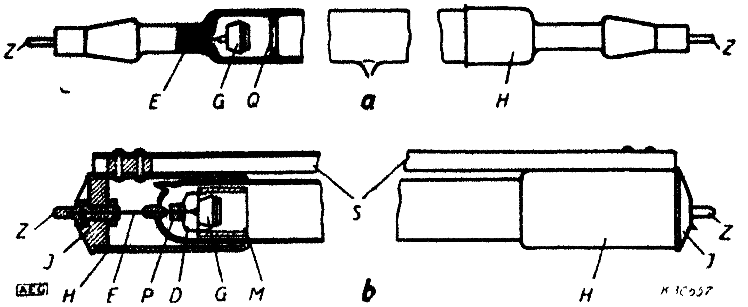

FIGURE 64. *a*. S, Burner of Quartz; *b*. S, Burner of I-G Phosphate Glass (Ende, *Z. technische Physik*.)

When the amount of mercury is such that no liquid or solid metal is present during operation of a lamp the static characteristic of the latter is not based upon the principles outlined in the previous chapters. Such lamps[11] are less affected by the temperature of the surroundings. As the load increases, the current increases markedly, but in contrast to the lamps described in Chapter 6 increase in voltage does not affect the operation of the lamp. The current can be adjusted by the series resistance rather than by ventilation, and the necessity for cooling is eliminated. The absence of the liquid mercury phase increases the stability of the lamp and also permits operation of the latter in any position. Bruijnes[12] pointed out that an excess of mercury might diminish the efficiency of a discharge tube by condensing on the walls and absorbing the ultraviolet. He described a discharge tube within which there was inserted a quartz tube. The latter was utilized to hold the material to be subjected to ultraviolet irradiation.

The lamp described by the Hanau Quarzlampen A.-G. uses special nickel-oxide-coated electrodes of basin-like members piled one on another. Argon at a few mm. pressure in the lamp serves to supply ions for conduction until the mercury, introduced as a small button of some hundredths of a gram sufficient to produce a vapor pressure of 700 mm. (corresponding to 350°C.), carries the discharge. Ignition is facilitated by the presence of a strip of Aquadag on the outside wall connected with the electrodes and interrupted in the neighborhood of one of them. This serves as a grounding device which collects electrostatic charges from the walls.[13] Very similar principles are employed in the therapy lamp (Alpina Heimsonne)[14] developed by that company. The therapy lamp is 10 to 20 cm. long and is enclosed in a special phosphate glass rather than in quartz. The glasses employed soften at 560°C. and, therefore, cannot stand the weight of masses of mercury but can be used with the self-igniting solid oxide electrodes which heat during the discharge. A millimeter of this glass transmits 34 per cent of the radiation of wave-length 2500A. When cool, the mercury condenses on the inner walls of the tube, the dimensions of which are so chosen that the discharge space is brought to 350°C. at its coolest spot, but nowhere exceeds 560°C. To secure this temperature, special pole-caps and metal protective mantles were placed about the electrodes to prevent the temperature of the glass in this region from approaching the softening point. The lamp is ballasted at 1.8 amperes, 120 volts burner tension for the 17 cm. arc, and worked at a point on the burner characteristic which, at 220 volts and 62 ohms, is still so far from the labile point that the discharge does not extinguish if the tension drops by 20 volts.

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[9] Buttolph, L. J., *Trans. Illum Eng Soc*, **28**, 153 (1933); **30**, 151 (1935). See also Hull, A. W., *Trans. Am. Inst. Elec. Eng.*, **47**, 753 (1928); Found, C. G., and Forney, J. D., *Ibid.*, 747.

[10] Moore, McFarlan, *Gen. Electric Review*, **23**, 577 (1920).

[11] British P. 399,317, October 5, 1933, to Quarzlampen-Gesellschaft m.b.H., Hanau.

[12] Bruijnes, J., U. S. P. 1,994,301, March 12, 1935, to General Electric Co.

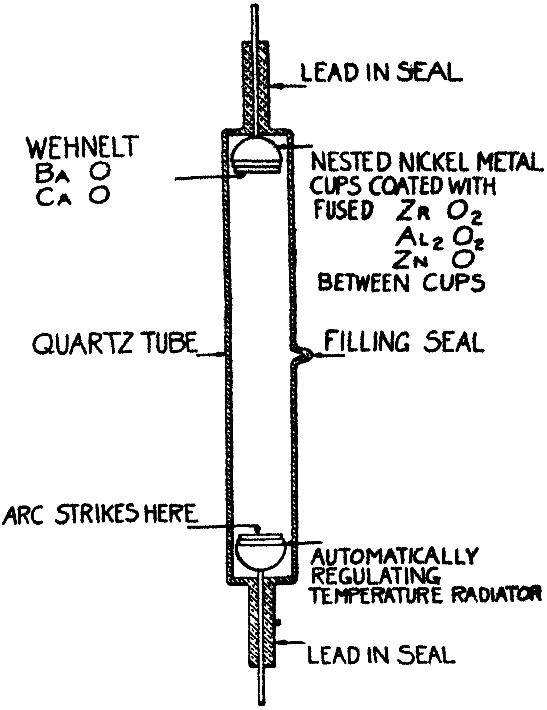
LEAD IN SEAL
WEHNELT BaO CaO
NESTED NICKEL METAL CUPS COATED WITH FUSED ZrO_2 Al_2O_2 ZnO BETWEEN CUPS
QUARTZ TUBE
FILLING SEAL
ARC STRIKES HERE
AUTOMATICALLY REGULATING TEMPERATURE RADIATOR
LEAD IN SEAL

FIGURE 65.

Quartz Burner Showing the Electrode Arrangement (Anderson and Bird, *Journal Optical Society of America*).

Figure 64 shows a section of the lamp. A glow electrode (G) sits on the sealed-in wire (E). The protective coat (M) is borne by two wires (D) joined

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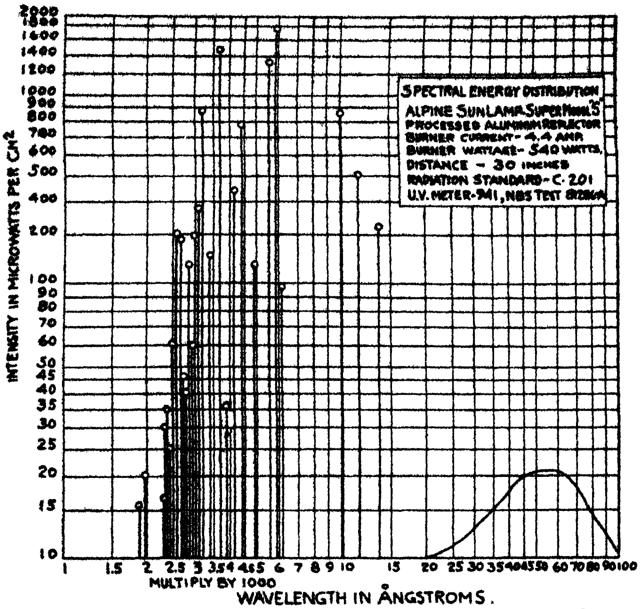
[13] See Spanner, H. J., U. S. P. 1,860,210, May 24, 1932.

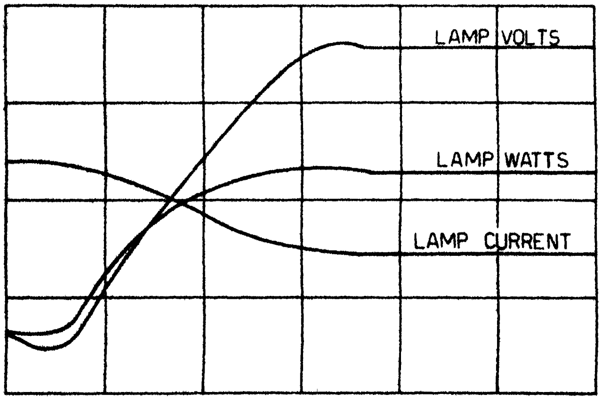
[14] Ende, W., *Z. tech. Physik,* **15**, 313 (1934).



Courtesy Hanovia Chemical and Manufacturing Co

FIGURE 66. Spectral Energy Distribution of Alpine Sun Lamp, Super Model "S."

to E, but insulated from E by glass (P) to prevent arcing to the mantle. The electrode is buried 10 millimeters within the mantle for better heat protection. The pole vessels are externally covered by a metal sheath (H), closed off by an insulating cover plate (I), through which the current is admitted, (Z). The two end sheaths

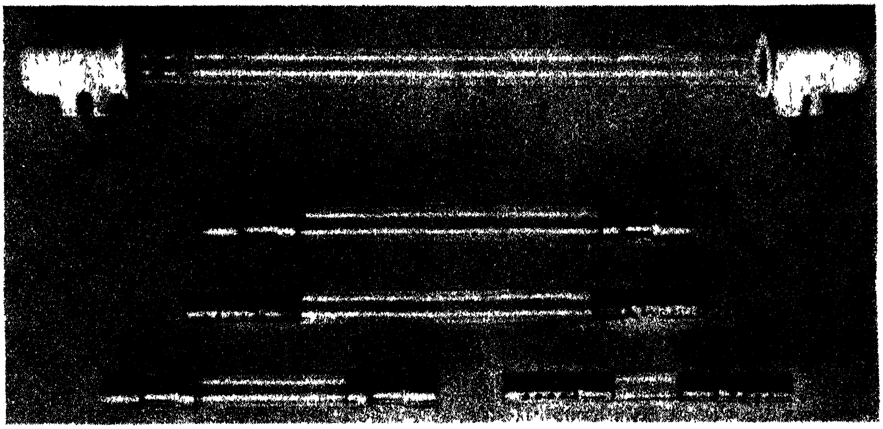


Courtesy General Electric Vapor Lamp Co.

FIGURE 67. Typical Starting Characteristics of 360-watt Uviarc.

are held by a long end-to-end shield which carries the whole burner. A transformer and accessory resistance are required. During starting, the voltage increases in proportion to the pressure for about six minutes, but there is a preliminary saddle due to irregularities in heating up various parts of the tube before the arc burns steadily, after which the characteristic follows the usual hyperbolic curve.

Anderson[15] uses a laminated electrode structure comprising pieces of metal separated by barium and calcium oxides. This principle is employed in the more recent models of the quartz lamp of the Hanovia Co. (Figure 65). The heat is radiated directly from the electrodes, which consist of a number of nested metal cups connected electrically and mechanically by a weld, and separated by the oxide coatings which automatically regulate the temperature. The 200-watt burner operates on 220 volts a.c., has a diameter of 16 mm. and an arc length of 130 mm. A ballast resistance or reactance must be used in series to limit the current. The life of the lamp is about 2000 hours. The spectral energy distribution of an Alpine Sun Lamp (Super Model S) at a distance of 30 inches is given in Figure 66. There was a processed aluminum reflector. The burner current was 4.4 amperes and its wattage was 540.[16]



Courtesy General Electric Vapor Lamp Co.

FIGURE 68. New Mercury Uviarcs.

Lamps of the newer type, which start automatically, reach stable operating conditions within about three minutes after starting. Figure 67 shows the typical starting characteristic of the 360 watt Uviarc.[17] The new lamps of the General Electric Vapor Lamp Co. operate in conjunction with a high reactance type transformer. The reactance limits the discharge current, stabilizes the arc and minimizes the flicker in the radiation output. The transformer may also supply a leading current at relatively high voltage from an extension of the primary winding to a power factor correcting capacitor.

The lamps are supplied in five sizes (Figure 68) consuming 150, 250, 360, 600 and 1200 watts. The radiation outputs of these burners at various wave-lengths in microwatts per sq. cm. at one meter are given in Table 12.[18]

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[15] Anderson, W. T., Jr., and Fraser, H. D., U. S. P. 1,890,926, Dec. 13, 1932; British P. 394,367 and 394,388; Anderson, W. T., Jr., U. S. P. 1,902,936, March 28, 1933; Anderson, W. T., Jr., and Bird, L. F., U. S. P. 2,006,081, June 25, 1935; *J. Opt. Soc. Am.*, 27, 95 (1937). Note also Siemens and Halske, A.-G., British P. 475,763, Nov. 25, 1937; *Chem. Abs.*, 32, 3279 (1938); Elenbaas, W., U. S. P. 2,116,741, May 10, 1938; *Chem. Abs.*, 32, 4891 (1938).

[16] Personal communication, Hanovia Chemical and Manufacturing Co. See also Melville, H. W., *Trans. Faraday Soc.*, 32, 1525 (1936).

[17] Unpublished data of Johnson, L. B., and Webster, S. B., communicated by the General Electric Vapor Lamp Co. See also Inman, G. E., and Lemmers, E., U. S. P. 2,085,530 and 2,085,531, June 21, 1937; *Chem. Abs.*, 31, 5698 (1937).

Table 12.—Radiation Output of Mercury Discharge Lamps.

Wave-length (Angströms)	Burner Watts 150	250	360	600	1200
	Microwatts per sq. cm. at 1 meter				
5780	37.3	60.2	83	255	510
5461	33.5	56.0	82	222	445
4358	28.5	45.5	72	192	385
4047	16.9	26.8	45	111	223
3654	49.6	78.5	122	327	654
3341	5.3	7.4	11.6	35	71
3129	32.6	50.8	85	203	406
3022	16.6	25.3	39.4	107	214
2967	8.8	13.5	20.9	56	113
2894	3.5	5.3	8.3	23	47
2804	7.0	10.9	15.7	42	85
2753	2.5	3.8	5.5	17	33.6
2700	3.0	4.4	7.6	20	40.2
2652	14.4	22.5	83.1	88	176
2537	15.5	27.8	47.4	103	207
2483	6.1	9.9	13.3	39	79.5

The 360-watt lamp with its transformer and reflector is shown in Figure 69. The 600- and 1200-watt tubes are intended primarily for industrial application where large, high-intensity sources are required.

The principle of the use of a discharge in mercury vapor at a low pressure in a noble gas frequently has been employed in sources intended for production of the resonance lines of mercury in physical laboratories. Pressure broadening of the mercury lines has been avoided by keeping the partial pressure of the mercury low. Kunze[19] warmed mercury to 40° C. in a glow discharge in neon, employing a capillary tube to secure great surface brilliancy, although this opened the possibility of broadening by the intermolecular fields of ions in high current density. Houtermans[20] secured high currents and great total brilliance by the use of a discharge tube with oxide cathodes, employing argon at 3-4 millimeters. This form of discharge (studied by Pirani[21]) is characterized by high strength and line sharpness. The discharge was started by a small induction coil or a medical high-frequency apparatus, it being necessary only to bring the high-tension electrodes near the lamp. The temperature of the mercury reservoir was regulated by placing the reservoir in a side-tube dipped in water. One part of the illuminating tube was compressed into a flat rectangle 30 millimeters square and 2 millimeters thick to maintain the discharge against the quartz wall and so lessen the effects of self-absorption. The width of the discharge depended upon the current, increasing with the latter at constant current density, but never completely covering the area of the rectangle. When the lamp was started, there was at first a self-maintained discharge, showing a Faraday dark space. In this state, the voltage drop over the lamp was high (180-200 volts) and the current but a few milliamperes, the lamp remaining cold. At a certain current value, the oxide cathode began to emit strongly, the voltage dropped to between 20 and 30 volts and the current rose. The current was not permitted to rise above 3.6 amperes to prevent the oxide cathodes giving off a dust which blackens the tube. During starting, however, the resistance could be momentarily removed, permitting a current of 4 to 4.5 amperes. At 24 volts and 2.6 amperes, the intensity could be kept constant within 2 per cent for over two hours. Such lamps could be used for some hundreds of hours without deterioration.

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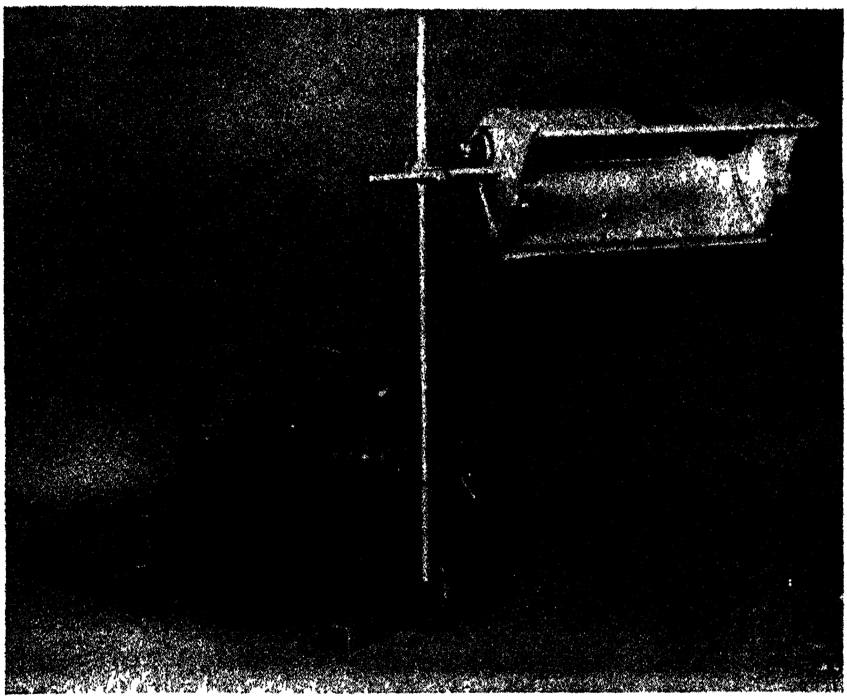
[18] Communication from the General Electric Vapor Lamp Co.

[19] Kunze, P., *Ann. Physik*, **5**, 793 (1930).

[20] Houtermans, F. G., *Z. Physik*, **76**, 474 (1932).

[21] Pirani, M., *Elektrotech. Z.*, **51**, 889 (1930).



Courtesy General Electric Vapor Lamp Co.

FIGURE 69. 360-watt Uviarc for General Laboratory Use.

Kornfeld and Müller-Skjold[22] devised a lamp which emits the line 2537A twelve times as intensely as does the usual mercury arc. The lamp operates at 220 volts and has water-cooled tungsten electrodes. The cathode is coated with a mixture of barium and strontium carbonates and is heated with current from a step-down transformer.

The Hanovia Co. now supply tubes in which 85 per cent of the emitted light is at 2537A. They are built to consume 30-100 milliamperes at 2000 or more volts. With an input of 25 watts, they supply 40 microwatts of 2537A radiation per square centimeter at 20 inches. They are available in various forms, straight, U-shaped and S-shaped, and usually have a tube length of from one to six feet. A form intended as a source for work on the Raman effect is shown in Figure 70.[23]

In one of the first lamps of this type, Wiegand[24] employed a discharge in nitrogen or carbon dioxide and some hydrogen at low pressures in a quartz or Uviol bulb containing a drop of mercury. The mercury extended the radiations from the limit of the nitrogen radiations (2800A) to about 2200A and improved the distribution of the spectral lines. The tube carried only 50 to 80 milliamperes, and operated at a temperature so low that it could be operated in direct contact with the material to be irradiated. Other forms, differing in structural features, have been described by Foulke,[25] who uses the negative glow between two closely spaced (0.5-2.0 mm.) oxide-coated nickel electrodes, in a gas containing neon (75 per cent) and helium (25 per cent) and a small quantity of argon at 30 mm. pressure. A small quantity of mercury is also present. The metastable potential of the major component is to be greater than the ionizing potential of the minor component. This lamp, contained in a fused silica or Pyrex container fitted with a base plug, is operated on 100-110 volts direct current or 75 volts alternating current. As a "getter" it contains a bead of alkali-metal oxide, hydroxide or carbonate. The lamp may be used for therapy, photochemistry, or ultraviolet signaling.

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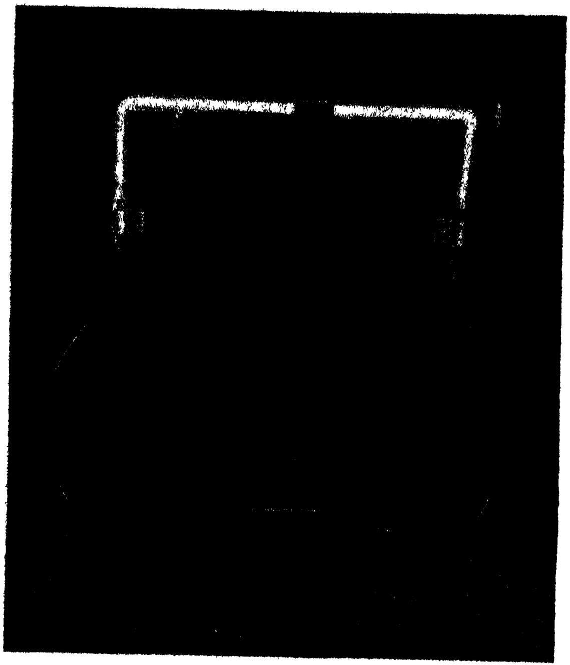
[22] Kornfeld, G., and Muller-Skjold, F., *Z physik. Chem*, **B31**, 223 (1936).

[23] See Leighton, P. A., and Leighton, W. G., *J. Chem. Ed.*, **12**, 139 (1935).

[24] Wiegand, K., German P. 509,373, Nov. 4, 1926; U. S. P. 1,971,887, August 28, 1934, to Patent-Treuhand-Ges. fur Elek. G m b H.; *Chem. Abs.*, **28**, 6371 (1934).



(Courtesy Hanovia Chemical and Manufacturing Co.)

FIGURE 70. Hanovia Sc-2537 Tube for Raman Work.

The G-1 or Glow Lamp of the General Electric Co. consists of two oxide-coated tubular filaments heated from within by tungsten filaments, a connecting and supporting bridge and center support to hold them, and a pool of mercury. It produces ultraviolet radiation by virtue of a glow discharge in the mercury vapor at low pressure throughout the entire bulb. Consuming approximately 40 watts, the lamp starts at a current of two amperes at 35 volts, and operates at 20 volts and two amperes. A separate small transformer is required for each lamp. It emits but little visible light.[26]

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[25] Foulke, T. E., British P. 361,394, July 21, 1931, to the British Thomson-Houston Co., Ltd.; U. S. P. 1,990,174-5, February 5, 1935, to General Electric Vapor Lamp Co.

A number of lamps have been patented by the Philips Lamp Works. In one form[27] of positive column discharge of mercury in argon at 5 millimeters the electrodes are led out at one end of the tube. Two anodes are separated by a screen and the supply wires of the incandescent oxide cathode are surrounded by insulating envelopes. The tube is widened where the supply wires are taken out for mounting in a device for irradiating flowing substances. A quartz tube with graded seal is employed. In another form,[28] the operating current density is maintained so low, either by use of a suitable voltage and a resistance in series with the discharge, or by the use of a suitable gas filling, *e.g.*, argon, that the temperature of the tube is below 100°, and the vapor of the mercury contained in the tube is less than 0.3 millimeter pressure. A lamp has been described[29] in which the anodes are carbon cylinders with leveled-off ends. An inner concentric quartz tube for irradiation fluids is embodied in the apparatus. To prevent disintegration products of the cathode from settling on the walls, grid-shaped anodes of gauze or parallel wires stretched on a frame are used to attract disintegrating particles without seriously interfering with the passage of the rays.[30] Devers[31] proposed the use of a loose powder of nitrides of boron, zirconium or titanium to reduce the deposition of cathodic materials on the walls and to react with any trace of water vapor present. A device embodying a reflecting mirror of chromium on the inner wall of the tube is due to Zecher.[32] Reynolds[33] described an apparatus in which a high-tension discharge in mercury vapor in argon or neon occurs in a quartz tube free from external protuberances, which is to be immersed in the substance to be irradiated. There is an electrode at one end of a tube with a lead-in wire fused to another tube situated concentrically within the outer tube and fused to the latter. One electrode is of mercury, the other of tungsten or steel. The whole high-tension discharge is symmetrically placed and the radiations pass through only a single thickness of quartz.[34]

Garrett[35] described a glow lamp for ultraviolet radiation for clinical or household use operated on 110-220 volt alternating or direct current without auxiliary equipment. The radiations are emitted by a polyatomic gas such as nitrogen at 2-3 millimeters pressure in admixture with argon, neon and helium at 1-2 centimeters. It was stated that the monatomic gases alter the spectrum of the nitrogen, increasing the proportion of ultraviolet. The monatomic gases also function in starting the discharge and in keeping the operating potential relatively low. Concentric grid-shaped electrodes of tungsten or molybdenum are employed in a quartz envelope, which contains also a strongly electropositive metal, alkali or alkaline-earth, which deposits on the electrodes and makes the lamp suitable for operation at 110 volts. Mercury may also be used in the lamp.

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[26] See also Lederer, K. and E., German P. 600,757, July 31, 1934.

[27] N. V. Philips' Gloeilampenfabrik, British P. 320,358, October 9, 1928; French P. 662,717, October 20, 1928; *Chem Abs.*, **24**, 270 (1930).

[28] British P. 299,704, October 22, 1928; N. V. Philips' Gloeilampenfabrik; *Brit. Chem. Abs.*, **B**, 246 (1930).

[29] British P. 299,931, November 8, 1928, to N. V. Philips' Gloeilampenfabrieken; *Chem. Abs.*, **23**, 3379 (1929).

[30] British P. 351,894, July 2, 1931, N. V. Philips' Gloeilampenfabrieken.

[31] Devers, P. K., U. S. P., 1,803,175, April 28, 1931.

[32] Zecher, G., U. S. P. 1,951,116, March 13, 1934; *Chem. Abs.*, **28**, 3279 (1934). See also British P. 381,084, September 29, 1932; 366,675, February 11, 1932, to Phillips Lamp Works.

[33] Reynolds, F., British P. 349,294, May 28, 1931.

[34] Many variations have been described. See, *e.g.*, Braselton, C. H., Ruben, S., Davies, L., and Harding, R., for a series of patents, U. S. P. 2,007,919-47, July 9, 1935, to Sirian Lamp Co.; Freedman, P., British P. 313,726-7, 1929; Geffcken, H., and Richter, H., British P. 265,636, May 3, 1928; Studienges. für Wirtschaft und Industrie, British P. 269,808, 1926; Kewley, F. E., and Balls, S. F., British P. 269,014, June 14, 1926. Even carbon electrodes have been proposed, British P. 410,706, 1934.

[35] Garrett, M. W., U. S. P. 1,783,643, Dec. 2, 1930, to Westinghouse Lamp Co.

A low-pressure mercury glow-discharge lamp, employing indirectly-heated unipotential oxide-coated electrodes as the source of electron emission to ionize the mercury vapor has been described by Marden and Nicholson [36] of the Westinghouse Co. It is necessary to use a transformer or a ballast lamp with the glow lamp to avoid overheating the electrodes. The voltage across the terminals of the glow lamp, and the resultant heating of the electrodes, decrease to a certain extent with increasing glow current, making the device self-regulating. The electrodes serve alternately as anodes and cathodes when used on alternating current. Such lamps have been made in sizes from those taking 0.2 to 0.3 ampere in half-inch bulbs one inch long to 30-ampere models in bulbs 3 to 12 inches in diameter. Figure 71 shows the indirectly heated electrodes and Figure 72 their mounting. The electrode around each heating coil is connected to the same lead-in wire as its respective coil. When the glow lamp is in series with a tungsten filament or other ballast on a 115-volt alternating current circuit, the voltage across the lamp is about 40 volts, until the electrodes are heated sufficiently to emit. During three to five seconds, the emission and glow-discharge increase and the lamp voltage drops to a point where the heating of the electrodes by the coils and by electronic and ionic bombardment maintains sufficient emission from the electrodes to sustain the glow-discharge current. During steady operation, about one-half of the current passes through the heater coils and the remainder is glow current. Marden and Nicholson gave data obtained with

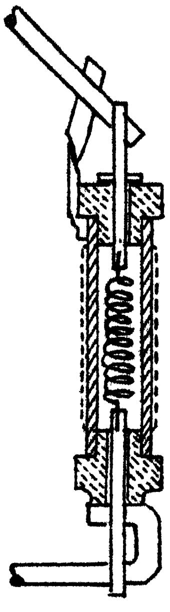

FIGURE 71 (Left).

Structure of Indirectly Heated Electrode of Marden and Nicolson. *(Transactions Illuminating Engineering Society).*

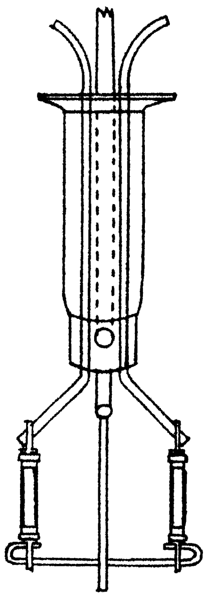

FIGURE 72 (Right).

Construction of Assembled Mount *(Transactions Illuminating Engineering Society).*

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[36] Marden, J. W., and Nicholson, M. G., *Trans. Illum. Eng. Soc.*, 26, 592 (1931); British P. 374,466, May 21, 1930; *Chem. Abs.*, 27, 3152 (1933).

a monochromator (uncorrected for reflection and absorption) comparing the energy distribution of the new glow lamp with those of the quartz mercury arc and the S-1 lamp. The percentage distribution of energy for the Corex glow lamp is about the same as for the mercury arc, except at the lower wave-lengths where the Corex glass absorbs the radiations. (See Chapter 10.) Of the total ultraviolet output, 90 per cent lies between 3132 and 2894A. On the other hand, Inman stated that, even through Corex, this glow lamp emits an amount of energy of the 2537A line which is undesirable for long-continued use. He believed that attempts to eliminate this would make the output between 2800 and 3100A negligible. Luckiesh pointed out that the S-1 lamp (see section on "dual-purpose" lighting) emits less of the 2537 line, since it operates under a higher pressure of mercury vapor.

Increasing the temperature or adding other gases such as argon concentrates the glow and diminishes the ultraviolet output. One, two, or possibly more of the lamps may be operated in series with a ballast which may be either a tungsten-filament lamp, an infrared heater, a choke coil, or a special transformer which can be concealed in a table lamp fixture.

Marden and Rentschler[37] claimed an improvement in the Marden glow lamp by making the heat-radiating capacity of the device great enough to maintain the internal temperatures between 20° and 75°C. The mercury reservoir is placed in a protuberance, with a more or less restricted opening, giving but a limited exposure of the mercury to the heat. This limits the mercury vapor pressure to 0.001-0.08 millimeter, which makes the emission of the 2537A line ten times as strong as the other lines. This point has also been emphasized by the Philips Lamp Works.[38] The desirability of increasing the output of this line obviously depends upon the purpose to which the lamp is to be put, a matter which will receive attention in subsequent parts of this book.

Prouty[39] described a portable compact power system including transformers, milliammeters, etc., for operating several quartz discharge tubes at high voltages and low currents (30-50 milliamperes). The tubes are of small diameter to reduce self-absorption of the resonance lines and yield intense short-wave ultraviolet radiations stated to be applicable for dental and surgical utilization.

Ultraviolet-emitting discharge tubes of quartz employing other emitting metals than mercury have been produced; sodium and magnesium have been proposed. Magnesium tends to impair the transparency of the tube. The Philips Works[40] proposed to preserve the transparency of the walls by coating that part of the wall intended for the passage of the rays with a substance (potassium chloride or fluoride or fluoborate in the case of magnesium) which either prevents deposition of the metal or renders the deposit transparent to the rays desired. Calcium fluoride may be used as a coating for the interior of a mercury vapor lamp. When the tube contains sodium vapor, the wall may be coated with sulfur or phosphorus. de Boer[41] places on some non-transmitting part of the bulb, a material which will adsorb the depositing substance and liberate it on heating. Carbon, calcium fluoride or zirconium oxide are suggested. The spectrum is emitted by iodine vapor in this tube.

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[37] Marden, J. W., and Rentschler, H. C., U. S. P. 1,917,848, July 11, 1933. See also Canadian P. 355,173,, Jan. 7, 1936. For more recent developments, see Marden, J. W., and Meister, G., U. S. P. 2,129,357, Sept. 6, 1938; *Chem Abs.*, 32, 8285 (1938).

[38] British P. 299,704, January 16, 1930, to N V. Philips' Gloeilampenfabrieken.

[39] Prouty, W. O., U. S P. 1,965,947, July 10, 1934; U S. P. 2,093,735, Sept. 21, 1937; *Chem. Abs.*, 31, 7773 (1937). See also Le Bel, C. J., U. S. P. 2,126,787, Aug. 16, 1938; *Chem. Abs.*, 32, 7836 (1938).

[40] British P. 336,222, July 5, 1929; 356,407, September 10, 1931; both to N. V. Philips' Gloeilampenfabrik.

[41] de Boer, J. H., U. S. P. 1,935,699, November 21, 1933; *Chem. Abs.*, 28, 693 (1934).

For mercury vapor, gold foil may be used. de Groot and Reerink[42] employ a member acting as a chimney above the path of discharge to carry off the vapor, which may settle on or combine with the chimney, a part of which is of gauze. This chimney is to be employed in a magnesium vapor lamp.

Tubes have been described in which the emission of ultraviolet radiations is caused by bombardment by electrons of a fluorescent substance on the electrodes or in a very thin film on the inner side of the wall of the quartz tube. Sulfides, selenides, oxides of the alkali or alkaline earth metals, boron compounds, etc., with small amounts of iron or mercury compounds incorporated, serve as emitters. Yttrium, lanthanum and gadolinium compounds increase the emission. The tube has a very low pressure gas or vapor filling. A grid-like anode accelerates the electrons emitted by the cathode. Visible radiations are emitted by the wire of the heater. A chromium or magnalium film on the opposite part of the bulb serves as a mirror.[43]

Materials within the envelopes of discharge tubes may also be excited by ultraviolet rays within the tubes to give blue or white fluorescent light.[44] In some of these zinc silicate, calcium tungstate and calcium molybdate form the internal coatings of the envelopes. A series of variously fluorescing layers is sometimes used. Fluorescent glass envelopes may also be employed.[45] Rare gas fillings[46] are sometimes used to the exclusion of mercury.[47]

DUAL-PURPOSE SOURCES

The proportion of the health-giving ultraviolet in the sun's radiations is small and varies greatly with the seasons and atmospheric conditions. It is greatly lessened by dust and smoke, so that in industrial communities and in cities very little may be available. Means have been developed for so altering the ordinary sources of illumination of homes, hospitals, schoolrooms, gymnasia, etc., as to enable them to provide also a supply of the desirable ultraviolet radiations. Illumination by such sources has come to be known as "dual-purpose" illumination, *i.e.*, visible illumination and simultaneous ultraviolet irradiation.

The engineering problems are concerned with the design and construction of a reasonably-priced source of ultraviolet within a lamp bulb supplying visible light and capable of operating from an ordinary lamp socket without the necessity of elaborate or expensive accessory equipment. From a therapeutic standpoint, the questions of wave-length range and intensity are paramount. It is necessary to choose for the envelope of the lamp bulb a material which will transmit visible light and ultraviolet radiations longer than about 2900 to 3000A and absorb those shorter than this limit, since the shorter rays are known to exhibit deleterious effects. As it is well known that excessive exposure to the sun's ultraviolet transmitted by the earth's atmosphere (longer than about 2950 to 3000A) may be harmful, it is necessary that the ultraviolet radiations emitted by a "dual-purpose" lamp be low in intensity since the lamps are used for considerable periods in ordinary home illumination. This explains the otherwise paradoxical nature of the claims of certain manufacturers that their bulbs emit only very low intensities of ultraviolet. A considerable field remains to be explored in order that the most suitable intensities and wave-length regions for effecting desired therapeutic ends may be firmly established. It is important that exact data be acquired regarding the effects of prolonged exposures to low intensities of the therapeutic range of the ultraviolet. Comparatively small amounts seem to be needed, at least for the prevention of rickets in chickens.[48] An industrial Cooper-Hewitt arc in glass affords some antirachitic protection, although not as much as one in Corex D glass, which, in turn, is somewhat less effective than one in quartz. Even 60- or 500-watt Mazda CX lamps, which have only a small ultraviolet output, have been recommended for long-continued use in poultry houses.[49]

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[42] de Groot, W., and Reerink, E. H., U. S. P. 1,905,688, April 25, 1933, to General Electric Co.

[43] Hummel, C., British P. 387,130, Feb. 2, 1933; Aicher, J. D., U. S. P. 2,109,984, March 1, 1938; *Chem. Abs.*, **32**, 3279 (1938); French P. 828,067, May 10, 1938, to Compagnie des lampes; *Chem. Abs.*, **32**, 6962 (1938).

[44] British P. 459,323, Jan. 6, 1937; 473,929, Oct. 22, 1937, *Chem. Abs.*, **32**, 2854 (1938); German P. 656,213, Feb. 1, 1938; British P. 476,240, Dec. 7, 1937; 485,875, May 26, 1938; *Chem. Abs.*, **32**, 8286 (1938), all to Patent-Treuhand-Ges. für elektrische Gluhlampen. See also Randall, J. T., British P. 466,503, May 28, 1937; *Chem. Abs.*, **31**, 7774 (1937); British P. 469,731-2, July 27, 1937; *Chem. Abs.*, **32**, 436 (1938), to General Electric Co., Ltd. Breadner, R. L., Randall, J. T., and Ryde, J. W., British P. 474,298, Oct. 28, 1937; *Chem. Abs.*, **32**, 2854 (1938); Randall, J. T., British P. 474,457, Nov. 2, 1937; *Chem. Abs.*, **32**, 2854 (1938). Rhodamine dyes may also be used, according to McKeag, A. H., and Randall, J. T., British P. 474,297, Oct. 28, 1937; *Chem. Abs.*, **32**, 3279 (1938); Jenkins, H. G., Ryde, J. W., and Wilson, G. H., British P. 483,846, April 27, 1938; *Chem. Abs.*, **32**, 6961 (1938); Jenkins, H. G., Canadian P. 375,310, July 26, 1938; *Chem. Abs.*, **32**, 6962 (1938); Randall, J. T., Canadian P. 375,308, July 26, 1938; *Chem. Abs.*, **32**, 6962 (1938).

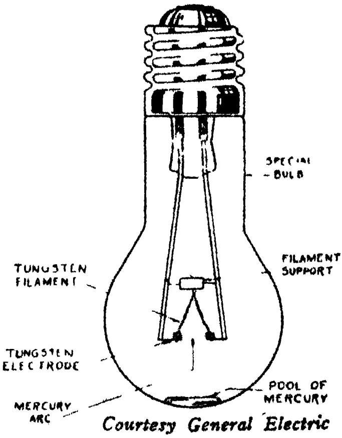
[45] French P. 808,048, Jan. 27, 1937, to Corning Glass Works; *Chem. Abs.*, **31**, 6434 (1937); British P. 476,945, Dec. 20, 1937, to I.G. Farbenindustrie, A.-G.; *Chem. Abs*, **32**, 4298 (1938); British P. 484,975, May 12, 1938, to N. V. Philips' Gloeilampenfabriken; *Chem. Abs*, **32**, 8286 (1938).

[46] French P. 810,298, March 18, 1937; *Chem. Abs.*, **31**, 8384 (1937); British P. 474,907, Nov. 9, 1937; *Chem Abs.*, **32**, 3280 (1938); French P. 822,815, Jan. 8, 1938; British P. 457,317; *Chem. Abs.*, **31**, 2946 (1937); all to Soc. anon. pour les applications de l'electricité et des gaz rares-etablissements Claude-Paz and Silva. Laise, C. A., U. S. P. 2,116,977, May 10, 1938; *Chem. Abs*, **32**, 4892 (1938); Fritze, O., Rüttenauer, A., and Wiegand, K., U. S. P. 2,103,032, Dec. 21, 1937; *Chem. Abs.*, **32**, 1193 (1938).

[47] For general discussions of this new type of fluorescent lighting which has the advantage of simulating daylight, see Claude, G., *Compt. rend.*, **203**, 1203 (1936); Servigne, M., *Ibid.*, 1247; Harrison, W., and Hibben, S. G., *Elec. World.*, **109**, 1530 (1938); Inman, G. E., and Thayer, R. N., *Elec. Eng.*, **57**, 245 (1938); von Ardenne, M., *Z. tech. Physik*, **19**, 41 (1938); Hibben, S. G., *Elec. J.*, **35**, 269 (1938).

FIGURE 73.

Sunlight (Type S-1) Lamp.



Courtesy General Electric Co.

One of the first bulbs for "dual-purpose" lighting was the S-1 sunlamp.[50] It comprises a combination of a mercury arc in argon between tungsten electrodes and an incandescent tungsten lamp in the same bulb, the latter of special glass of low iron content to transmit radiations from 2800 to 3100A.[51] Figure 73 shows the structures within the bulb. No tilting is required to start this lamp. When the filament is lighted, the arc strikes across the filament terminals and disposes itself across the main electrodes. A wide range of operating angles is possible. A low-voltage supplied by a transformer with a special volt-ampere characteristic is essential to the operation of this lamp, which consumes approximately 400 watts. The no-load voltage of the secondary of the transformer is approximately 35. When the switch is closed, the filament takes about 9 amperes and the drop across it is about 33 volts. The mercury arc starts in parallel, the voltage drops to eleven volts, and the total current through both arc and filament is 30 amperes. In operation, the arc supplies about one-fourth of the light, two-thirds coming from the tungsten electrodes, the color temperature of which is above 3500°K. The lamp is said to be twenty times more effective than summer sunlight. A frosted bulb is used, and the coiled filament is inverted and located above the electrodes. In another model, S-2, the arc length is increased, and a metal cap of aluminum is placed over the lower portion of the bulb to minimize glare and to redirect much energy back into the mercury vapor area, increasing the operating temperature. As a result, the lamp emits about one-half as much ultraviolet as the S-1 model, while consuming only 40 per cent as much energy. The lives of the S-1 and S-2 lamps are shortened by both over- and under-voltage operation.[52] Porter, Egeler and Sturrock [53] have tabulated electrical and other physical data regarding these sources. Luckiesh has pointed out that the high mercury-vapor pressure of these lamps leads to a high degree of absorption of the 2537A line, long-continued exposure to which would be dangerous.

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[48] Hughes, J. S., and others, [*Trans. Ill. Eng. Soc.*, April, 1927]; cited by Buttolph, L. J., *Trans. Ill. Eng. Soc.*, **26**, 583 (1931).

[49] Anon., *Trans. Ill. Eng. Soc.*, **26**, 551 (1931).

[50] Luckiesh, M., *Gen. Electric Rev.*, **33**, 89 (1930); Forsythe, W. E., *et. al.*, *Gen. Elec. Rev.*, **33**, 358 (1930); Luckiesh, M., *Elec. World*, **94**, 835 (1929); **95**, 300 (1930); *Trans. Ill. Eng. Soc.*, **25**, 397 (1930); Gordon, N. T., and Benford, F, *Gen. Elec. Rev.*, **33**, 283 (1930); Forsythe, W. E., and Christison, F., *Ibid.*, **32**, 662 (1929).

[51] Strickland, R. F., British P. 147,292, 317,832, 375,477 (1932), to British Thomson-Houston Co., Ltd. Strickland, F., Blake, H. D., and McLean, S., British P. 398,290, September 14, 1933. See also British P. 383,342, November 17, 1932, to Zaidan-Hojin Aoyagi Kenkyusho, for a method of starting a similar lamp.

The spectrum emitted by the tungsten-mercury arc, according to Forsythe and Easley,[54] shows a continuous radiation from 4000 to 2100A. When the temperature is increased by external heating, the increased mercury vapor pressure causes the mercury absorption bands to appear. The 2540 band is 0.1A wide at 220°C. (vapor pressure 32 mm.) and with increasing temperature spreads to longer wave-lengths, reaching 2576A at 407°, and 2652A at 426°C. At 350°C., the resonance line disappears, being replaced by two narrow bands at 2534 and 2532A which at higher temperatures merge with the 2540A band. At 426°C., there is continuous absorption between 2530 and 2652A, with evidence of further absorption beyond 2652A. Five fluted bands around 2345A appear between 320° and 340°C. and broaden until they cover 16A at 420°C. Pressure causes the disappearance of some lines between 3500 and 2100A. These effects are somewhat different from those exhibited by mercury vapor in an absorption cell.

During the first few seconds of operation, the S-1 lamp emits some argon lines, but after a few minutes only mercury lines are detected.[55] Similar effects are observed if the argon is replaced by helium neon, nitrogen or carbon dioxide. When hydrogen is the gas present, the lamp continues to radiate bands characteristic of mercury hydride, along with several other bands at shorter wave-lengths.

Other data on the radiations emitted by the General Electric Sunlamp have been published by Benford,[56] Coblentz [57] and Barnes.[58] Barnes gave the average energy flux values of a number of lamps for the principal mercury lines between 2500 and

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[52] Oday, A. B., and Porter, L. C., *Trans. Ill. Eng. Soc.*, **28**, 121 (1933).

[53] Porter, L. C., Egeler, C. E.. and Sturrock, W , *Trans. Ill. Eng. Soc.*, **27**, 23 (1932).

[54] Forsythe, W. E., and Easley, M. A., *Phys. Rev.*, **36**, 150 (1930).

[55] Dooley, D., *Phys. Rev.*, **36**, 1476 (1930).

[56] Benford, F., *J. Motion Picture Eng.*, **14**, 414 (1930); Gordon, N. T., and Benford, F., *Gen. Electric Rev.*, **33**, 290 (1930).

[57] Coblentz, W. W., *J. Am. Med. Assn.*, **95**, 411 (1930).

[58] Barnes, B. T., *Phys. Rev.*, **36**, 1468 (1930).

6000A, and for the continuous spectrum up to 17,000A, determined by thermopiles and galvanometer, with a quartz prism monochromator which received on its slit energy from all parts of the arc and the electrodes. The line and continuous emissions were separated by taking readings both at the lines and at intermediate points, plotting continuous curves from the latter, and deducting the continuous curves from the values taken at the lines. The continuous curve was possibly too high below 4500A because of the inclusion of less important mercury lines, while the opposite was true in the red and infrared regions.

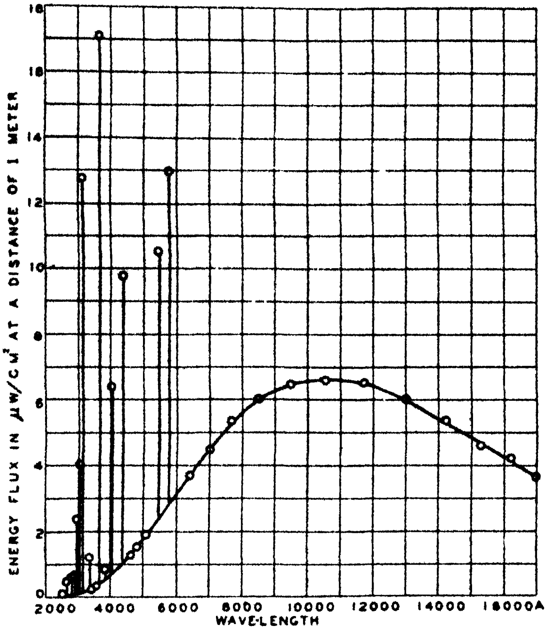

FIGURE 74. Energy Flux (μw/cm^2) One Meter from Center of Arc (General Electric Sunlamp) in a Direction Normal to the Plane of the Leads. Lamp burning without reflector with 115 volts on the primary of the transformer Average lamp current and voltage 30.9$_6$ amps and 10.6 volts. Curve represents energy in 50A band of continuous spectrum. Heavy lines above the curve give energy flux in lines or groups of lines in arc spectrum (B. T. Barnes, *Physical Review*).

In Figure 74 the intensities in microwatts per square centimeter at one meter distance in a direction perpendicular to the plane of the leads are given for an average of 26 lamps, operated with 115 volts on the primary of the transformer. The peak of the curve lies at about 10,600A, quite close to the maximum in the curve for the energy radiated by tungsten at 2500°K. The shape of the curve below 5000A, however, is approximately that for tungsten at 3250°K., the temperature of the hottest parts of the electrodes. The output of visible and ultraviolet radiations was much too high in comparison with that of the infrared for tungsten at 2500°K., a fact explained by the composite nature of the continuous radiation, the electrodes (above 3000°K.) giving a relatively high proportion of visible and ultraviolet, while the filament and the incandescent parts of the leads at much lower temperatures, but with a larger area, give much of the infrared, and shift the maximum to longer wave-lengths.

The average total energy flux at one meter is 2380 microwatts per square centimeter (10.6 volts and 30.95 amperes). Table 13 gives the average energy flux for each of the principal mercury lines, and the corresponding per cent of the average total energy flux.

Table 13.—Energy Flux of Mercury Lines.

Wave-length of line, A	Microwatts per cm.²	% of total	Wave-length of line, A	Microwatts per cm.²	% of total
5780	$9._7$	0.4	3130	$13._5$	0.5_7
5461	$8._2$	0.3_4	3024	4.4_0	0.1_9
4358	$9._0$	0.3_8	2967	2.5_4	0.10_7
4047	$5._9$	0.2_5	2894	0.7_1	0.03_0
3905	$0._4$	0.01_7	2804	0.6_9	0.02_9
3650	$17._4$	0.7_3	2650	0.6_5	0.02_7
3342	$1._1$	0.04_6	2537	0.1_2	0.00_5

The distribution between line and continuous spectral energy in various broad wave-length regions is given in Table 14.

Table 14.—Distribution Between Line and Continuous Spectral Energy.

Microwatts per cm.²	2500-3200A	3200-4000A	4000-7600A	7600-17,000A	17,000A
Line spectrum	$22._6$	$18._9$	$(32._7)$*	....	....
Continuous	$0._6$	$5._2$	209.	....	....
Both	$23._2$	$24._1$	242.	1090	1000

* Red lines in the mercury spectrum included with the continuous spectrum

The continuous spectrum furnishes less than 3 per cent of the energy below 3200A, but over 86 per cent of the visible. Since much of the continuous spectrum is in the red end with low visibility, the continuous spectrum furnishes only 76 per cent of the light radiated perpendicular to the plane of the leads. Of the total, one per cent is radiation of wave-length less than 3200A, one per cent is between 3200 and 4000A, and 10 per cent lies in the visible. That less than 3000A is only 3 per cent of the total emitted energy.

The results are in fair agreement with those of Benford, although the compositions of the bulbs have been changed. Different lamps vary widely in regard to the emission of the 3650A line, the intensity of which often increases over 50 per cent during the first 40 hours of burning. Benford found 28 per cent higher values for the energy between 4000 and 7000A (185 microwatts per square centimeter), a divergence for which no explanation could be given. The results are not comparable with those of Coblentz whose measurements were made upon the whole lamp unit, including a reflector. Under these conditions, the temperature of the mercury pool is 7° higher and the output below 3200A might be expected to be 10 to 15 per cent greater.

There have been other types of lamps proposed for "dual-purpose" lighting. The bulb of Corex (or Pyrex) may contain a mercury globule and oxide-coated electrodes to produce the ultraviolet-emitting glow discharge that fills the bulb at low temperature, while a sealed inner bulb provided with a tungsten filament serves both as a ballast resistance for the mercury vapor discharge and as a source of light.[59]

[59] Inman, G. E., British P. 390,384, April 6, 1933, to British Thomson-Houston Co., Ltd.

[60] Oosterhuis, E., U. S. P. 1,951,106, March 13, 1934, to General Electric Co. See also Craig, P., U. S. P. 1,798,658, March 31, 1931.

Oosterhuis[60] has described a reading lamp, with a standard containing the necessary transformers, which may comprise a helically wound glower for infrared and visible light, ultraviolet being supplied by a discharge between an incandescent cathode and two anodes in argon at a few millimeters, the tube containing some liquid mercury. The two sources employ separate circuits, each with a transformer, and are usable independently. Sperti[61] placed the arc and the filament in separate chambers.

Other attempts to produce "dual-purpose" illumination include utilization of a combination of separate quartz mercury arcs of usual form, and lamps for visible light in one fixture, provided with reflectors, filtering windows, and provisions for ventilation.[62] There has also been a considerable development of reflectors and accessory fixtures for the application of the S-1 Sunlamp. Oxidized or polished aluminum and polished chromium are among the more effective reflecting materials for ultraviolet between 2800 and 3200A.[63] Details of installations for homes, schools, offices, gymnasia, swimming pools, etc., have been described.[64]

METALLIC VAPOR ARCS OTHER THAN THE MERCURY TYPE

The dependence of the intensity and efficiency of radiation in metal vapors on pressure is similar for mercury, cadmium and zinc.[65] At the time of the development of the mercury-vapor arc, Stark and Küch[66] examined Heraeus quartz lamps having electrodes of metals and metalloids. The lamps were made in both of the forms indicated by Figures 75 and 76. Most of these lamps are of little practical interest because of the difficulty of starting, although developments of the cadmium

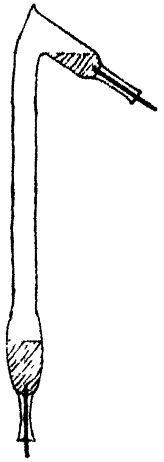

FIGURE 75.

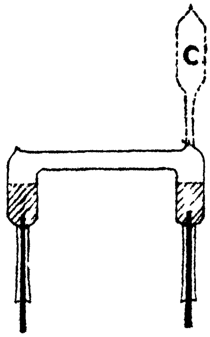

FIGURE 76.

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[61] Sperti, G., British P. 396,210, August 3, 1933.

[62] Rolph, F. W., U. S. P. 1,945,567, February 6, 1934, to Holophane Co. Paget, R. A. S., U. S. P. 1,943,877, January 16, 1934, to Thermal Syndicate.

[63] Coblentz, W. W., and Stair, R., *Bureau Standards J. Res.*, **4**, 189 (1930); Luckiesh, M., and Taylor, A. H., quoted by Porter, L. C., Egeler, C. E., and Sturrock, W., *Trans. Ill. Eng. Soc.*, **27**, 30 (1932).

[64] Oday, A. B., and Porter, L. C., *Trans. Ill. Eng. Soc.*, **28**, 121 (1933).

[65] Fabrikant, V. A., *Bull. acad. sci. U.R.S.S., Classe sci. math. nat. Ser. phys.*, 441 (1936); *Chem. Abs.*, **31**, 2925 (1937).

[66] Stark, J., and Küch, R., *Physik. Z.*, **6**, 438 (1905).

arc have excited interest. The outer diameter was 0.9 centimeter, the length of the form shown in Figure 75 was 13 centimeters and of that shown in Figure 76 was 9 centimeters. Nickel rods served to conduct the current to anode and cathode. The lamp was charged with metal by means of the container C shown in Figure 76. This container was filled with molten metal and on evacuation of the tube the metal passed into the lamp tube, after which the container C could be removed by fusing the narrow part. The lamp was pumped out thoroughly while in operation in order to get a satisfactory vacuum. The lamp was started by a spark from an induction coil, the metal being heated by a gas blast-lamp until sufficient metal vapors had been produced to cause an arc to form. A voltage of 100-200 was used.

The cadmium lamp was easy to start and operated at 2 to 5 amperes with metal-cooling; with water-cooling it could be operated at 8 amperes. The zinc lamp was more difficult to start and required heating with a blast lamp in order to put it into operation. With metal-cooling it operated at 3 to 5 amperes. The lead lamp required very intense heating in order to start. With water-cooling it operated at 8 to 10 amperes producing a strikingly rich spectrum. The bismuth lamp also required intense heating when starting and with water-cooling could be run at 7 amperes. The antimony lamp on the contrary was easily lighted and burned at 3 amperes, and did not require water-cooling unless a very strong current was employed. The spectrum covered a very wide range so that bodies exposed to the light from this lamp more nearly resembled their normal daylight color than when mercury or similar metallic arcs were employed. The antimony arc gave rise to very strong fluorescent effects, sodium glass fluorescing strikingly with a greenish-yellow color, while lead glass exhibited a blue fluorescence. Tellurium and selenium lamps were also tested. The former was operated at 6 amperes. The selenium lamp offered difficulties in starting. A form of cadmium arc lamp, that of Lowry and Abram,[67] shown in Figure 77 maintains the arc between water-cooled electrodes of solid cadmium. This cooling is important, partly because it checks the vaporization of the metal, but mainly because if the metal is allowed to melt it is liable to crack the tube whenever the lamp is started or stopped.

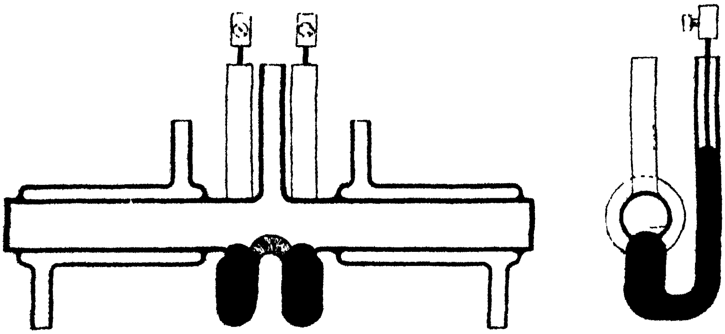

FIGURE 77. Cadmium Lamp.

The lamp is operated in conjunction with a Gaede pump, as the metal gives off considerable quantities of gas under the influence of the electric discharge, and this gas must be pumped off in order to maintain the vacuum. Occasionally, when the vacuum is good, the arc will start itself on merely switching on the current, but usually it is necessary to start the arc by a spark. This can be done conveniently by connecting the electrodes to the inner walls of two Leyden jars and connecting the outer walls to the secondary terminals of an induction coil. The light emerges through two windows of quartz. In one form of the lamp these windows are protected from condensed metal by water-jacketing the ends of the tube to which they are attached, but the water-jacketing must not extend to the central part of the tube. The latter must remain hot in order to prevent the formation of a conducting bridge of condensed metal. An arch of silica is provided to bring the arc to the center of the tube. The cadmium arc will burn quite well under a pressure of 100 volts, but it has a longer life if the voltage is higher, owing to the fact that an arc of greater length can be kept alight. The extinction of the lamp on the lower voltages is caused most frequently by the distillation of cadmium from the electrodes, which thus become shortened unduly.

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[67] Lowry, T. M., and Abram, H. H, *Trans. Faraday Soc.*, 10, 103. Note Bates, F. J., *Phil. Mag.*, 39, 353 (1920).

Stammreich [68] describes a metallic vapor lamp using cadmium amalgam in which a condenser is connected to the arc tube for collecting metal distilled from the latter. In some instances [69] mercury may be distilled from the amalgam to a separate compartment which is then closed before the cadmium begins to vaporize. The mercury is afterward run back by tilting the lamp.

Nagaoka and Sugiura [70] have reviewed the development of cadmium lamps with emphasis on the deficiencies of the previous types. They describe a lamp which comprises a tube with fused quartz cylinder surrounded with molybdenum or tungsten wire, the latter heated by electric current which can be raised to the required temperature. A second fused quartz cylinder is placed above the first cylinder, suspended by a holder which has a hole permitting light to pass through a window placed at the end of the side arm. The cadmium vapor is produced in this cylinder. The luminous particles can be concentrated in a second cylinder to obtain great intensity of light and the density of the cadmium vapor can be controlled by heating the coil around the first cylinder. A cathode of coiled tungsten is used to concentrate electronic currents through the cadmium vapors toward the molybdenum anode. Electric potential of 100 volts and electronic current of 0.3 to 4 amperes between cathode and anode are sufficient to excite cadmium vapors at 300° and to obtain intense and stable light. The tube is constructed of double glass and is water-cooled.

Other cadmium amalgam discharge tubes have been described by the N. V. Philips' Gloeilampenfabriken.[71] Krishnamurti [72] has found a cadmium-tin alloy arc a suitable source for the excitation of Raman spectra. The lines 5085.8 and 6438.5A are particularly effective.

Because of its wider spectral extension in the visible, the cadmium-mercury vapor lamp has attracted much attention for general illumination, but this is not within the province of this book.[73]

A drawback to the use of cadmium- or zinc-enclosed arcs has been their short-ness of life. The metals even when pure tend to adhere to the walls, and break the latter on cooling. Bates[74] found the addition of a small proportion of gallium to lessen this tendency in the case of cadmium. As he found it difficult to obtain pure gallium, he later employed tin instead, using a 50-per cent alloy of cadmium and tin, which melted at 176-200°C.[75] The arc used was of the Cooper-Hewitt type; the low vapor-pressure of the tin made the light almost entirely that of cadmium. It has since been stated that the gallium exerted its beneficial effects by virtue of its own impurities. Bismuth, lead or thallium are also effective, but should be limited to less than 1 per cent of the total filling.[76] The deterioration of the quartz envelopes of high-pressure lamps has been ascribed to attack by positive ions of the metal vapor, which have greater chemical activity than the atoms. This deterioration the Siemens-Halske Co.[77] propose to obviate by covering a part of the wall near the bulb or portion of the arc in which considerable potential drop occurs by an openwork metallic structure of spiral or braid or metal strips placed edgewise and not connected to a source of potential.[78]

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[68] Stammreich, H., British P. 294,172, July 19, 1927.

[69] Stammreich, H., French P. 657,426, July 11, 1928; U. S. P. 1,828,346, October 20, 1931.

[70] Nagaoka, H., and Sugiura, Y., *Sci. Papers Inst. Phys. Chem. Research (Tokyo),* **10**, 263 (1929); *Chem. Abs.*, **23**, 5118 (1929).

[71] British P. 336,208, July 5, 1929, to N. V Philips' Gloeilampenfabrieken; Elenbaas, W., Canadian P. 371,090, Jan. 11, 1938; *Chem. Abs.*, **32**, 2854 (1938); Elenbaas, W., and Jonas, G. B., U. S. P. 2,116,742, May 10, 1938; *Chem. Abs.*, **32**, 4891 (1938).

[72] Krishnamurti, P., *Indian J. Physics*, **5**, 587 (1930). *Chem. Abs.*, **25**, 1159 (1931).

[73] Spanner, H. J., *Trans. Illum. Eng. Soc.*, **30**, 178 (1935); *Chem. Abs.*, **29**, 5359 (1935). For a general discussion of recent electric vapor lamps, see Malley, R. D, *Elec Eng.*, **53**, 1447 (1934), and Marden, J. W., Beese, N. C, and Meister, G., *Trans. Illum. Eng. Soc.*, **32**, 84 (1937).

A cadmium amalgam arc, especially intended as a source for the preparation of vitamin D,[79] is designed to avoid breakage on cooling by so arranging that on interruption of the discharge, the tube is automatically put in such a position that the free surface of the substance yielding the vapor is larger than when the lamp is in the working position. Carbon electrodes are used in a lamp employing a discharge in cadmium vapor mixed with nitrogen and hydrogen or a rare gas, and designed for television, the excitation of fluorescence, and for therapy.[80]

The Siemens and Halske Co.[81] proposed to stimulate the growth of plants by a lamp which emits predominantly in the region 3300 to 3600A. That such rays would prove effective was based upon the claims (by no means generally accepted) of workers with mitogenetic rays that dividing cells give out radiations of wave-length 3400A. This region was also claimed to be useful for healing purposes because of an alleged destructive action on virulent tumors. That sunlight lacks this property was claimed to be due to an antagonistic action of even low intensities of radiations in the wave-length region 3200 to 2900A. For the lamp, there was suggested an arc in quartz, one electrode being silver or zinc. The arc was to be drawn out as far as possible by a moving gas jacket. The intensity of the crater was to be reduced by fins or by water-cooling, the light from the center of the arc only being used. A filter for suppressing radiations of wave-lengths less than 3200A was also employed. Also an arc in vapors from alloys of the zinc group, such as zinc (17 per cent), cadmium (83 per cent) was proposed.[82]

Mitchell[83] compared three methods of securing the resonance lines of cadmium or zinc for use in physical studies of fluorescence. The methods utilized were the high potential discharge in a mixture of helium and zinc vapor,[84] a discharge tube of the Schüler type[85] with hollow cathodes, partly filled with zinc and an arc with hot equipotential, oxide-coated cathode; he found the latter to be the most economical and convenient. The arc was formed in a bulb filled with a helium discharge, and enclosed in a furnace with quartz windows, to vaporize a supply of zinc. The zinc lines began to appear at 330°C. At 370°C., the arc constricts and the helium is pumped out.

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[74] Bates, F., *Bureau Standards Sci. Paper No. 371* (1920).

[75] Bates, J. R., and Taylor, H. S., *J. Am. Chem. Soc.*, 50, 771 (1928).

[76] British P. 372,843, May 19, 1932, to Siemens and Halske, A.-G.

[77] British P. 397,680, August 31, 1933, to Siemens and Halske, A.-G.

[78] For details of the static characteristics of the high-pressure cadmium arc, see British P. 404,341, January 15, 1934, to Siemens and Halske, A.-G.

[79] British P. 366,366, February 4, 1932, to N. V. Philips' Gloeilampenfabriken. See also Elenbaas, W., and Jonas, G. B, U. S. P. 2,116,742, May 10, 1938. *Chem. Abs.*, 32, 4891 (1938).

[80] British P. 418,128, October 18, 1934, to General Electric Co., Ltd., and Patent-Treuhand.

[81] British P. 296,724, February 24, 1930, to Siemens and Halske, A G. Silver-leaf filters transmitting between 3050 and 3300A, may be employed in the envelopes, according to C. J. Milner, British P. 485,787, May 25, 1938, to British Thomson-Houston Co.; *Chem. Abs*, 32, 7835 (1938).

[82] British P. 306,112, February 27, 1930, to Siemens & Halske Co.

[83] Mitchell, A. C. G., *J. Frank. Inst.*, 212, 305 (1931).

[84] Ellett, A., *J. Opt. Soc. Am.*, 10, 427 (1925).

A xenon lamp has been described as a source of light in the extreme ultraviolet by Harteck and Oppenheimer.[86] The lamp is said to yield through a fluorite window the resonance lines of xenon at 1469 and 1295A. It can be operated for several hundred hours.

MANUFACTURE OF QUARTZ PRODUCTS

Two scientific and engineering leaders had the foresight to grasp the industrial possibilities of the large-scale production of fused quartz, Prof. Elihu Thomson of the General Electric Co. at Lynn, Massachusetts, and Sir Richard Paget in England. Under their leadership, the experimental work developed independently in both countries. In England, the latter organized the Thermal Syndicate in 1903, which carried out early development under the direction of Hutton[87] and Dr. J. F. Bottomley. An account of the early work has been published by Paget.[88] The Syndicate early made opaque and translucent fused silica by fusion of glassmakers' sand. In 1906, the Silica Syndicate, Ltd., of London, worked patents of Kent and Lacell for the manufacture of transparent quartz glass. Other developments occurred in Germany, where Heraeus extended the work to the production of the tubes of mercury vapor lamps and Voelker founded a company in 1908, and in France where two companies, Le Quartz Fondu and Quartz et Silice have been producing since the war. The remarkable properties of this acid-resistant material, low solubility and low thermal expansion, made it of great importance to chemical and electrical industries and stimulated the large-scale development of the industry.[89]

The advances in America under the direction of Elihu Thomson in the Thomson Research Laboratory of the General Electric Co. at Lynn have been more closely concerned with the production of articles of clear or transparent quartz, for optical apparatus and for the transmission of ultraviolet radiations, the experimental work on which is largely due to Dr. E. R. Berry, P. K. Devers and L. B. Miller, although the opaque or coarser variety has also been developed by Mr. H. L. Watson. An account of the Lynn developments has been given by Dr. Thomson on the occasion of the presentation to him of the Franklin Medal of the Franklin Institute.[90] General reviews of the recent developments of the industry have been written by Moore[91] and Ibakh.[92]

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[85] Schüler, H., *Z. Physik*, **35**, 323 (1926).

[86] Harteck, P., and Oppenheimer, F., *Z. physik Chem.*, **16B**, 77 (1932); Groth, W., *Z. Elektrochem.*, **42**, 533 (1936).

[87] Hutton, R. S., *Trans. Am. Electrochem. Soc.*, **51**, 49 (1927).

[88] Paget, Sir R., *J. Roy. Soc. Arts*, April 4, 1924.

[89] Winship, W. W., *Trans. Am. Electrochem. Soc.*, **50**, 177 (1926).

[90] Thomson, E., *J. Frank. Inst.*, September, 1925.

[91] Moore, B., *Chemistry and Industry*, **50**, 671 (1931); *Trans. Ceram. Soc.*, **31**, 217 (1932); **32**, 45 (1933).

[92] Ibakh, B., *Keram. Steklo*, **8**, No. 8, 9 (1932) (Russian developments); *Chem. Abs.*, **27**, 821 (1933).

Chapter 9

Sources of Continuous Ultraviolet Radiations for Absorption Studies

In the measurement of ultraviolet absorption spectra, it is desirable that the source of illumination be continuous, or if that condition cannot be attained, the source should at least give a great number of closely spaced lines, so that there may be radiations of practically all wave-lengths available for absorption in the region studied. It is readily apparent that it would be futile to attempt to obtain the fine structure of an absorption band with the mercury arc as a source, since there are wide gaps in which no observations could be made.

One method of attaining this object would be to utilize as electrodes a number of metals, each of which emits many lines. The nature and amounts of the metals should be so chosen that gaps in the spectrum of one are filled by lines from the others. Such a source has been developed for the visible region.[1] The lines are not only closely spaced but are of very nearly equal intensity, so that the weaker ones can be photographed without overexposing the stronger ones. The electrodes are of carbon coated over with a fused mixture of the oxides of vanadium, titanium and molybdenum. The method is not, however, available as yet in the ultraviolet region. For measuring the broad fused systems of absorption bands of substances in condensed systems, that is, of liquids or of solutions, especially where a very high degree of quantitative accuracy is not required, the source of the ultraviolet radiations may be either the iron or the tungsten spark, both of which have many lines. Where it is desired to bring out the finer structure of the absorption bands, particularly in the case of gases, recourse is had to underwater sparks, to incandescent filament lamps burned at high voltage, to cathode-ray bombardment lamps, or to the hydrogen discharge tube.

Underwater Sparks. It has long been known that an arc can be made to burn and that sparks can be passed under liquids. In 1851, Masson[2] found the under-liquid arc to emit chiefly a continuous spectrum, although in the case of many metals, it has since been shown that there is superposed upon the continuous spectrum a bright-line spectrum. The underwater sparks from a large induction coil, between many metals, were studied by Wilsing,[3] who observed that some of the lines were reversed, that is, wholly dark, or bright but marked by a darkened center. The reversals are due to the absorption of emitted radiations by some of the metal vapor or by colloidal metal dispersed in the water. Being excited when dispersed, the atoms are in a condition to absorb many lines. The study of these reversals has been an aid in the classification of the lines of various metals.[4] Arcing or sparking metals under liquids is one of the standard methods of dispersing the metals to form colloidal suspensions. Because of the turbidity thus produced, an arrangement for circulating the water must usually be provided when the underwater spark is employed as a source for absorption spectrophotography.

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[1] Eppley, M., *J. Frank. Inst.*, **201**, 233 (1926). Some of the new fluorescent lamps discussed in Chapter 8 may be of value as spectroscopic continuous sources for the visible and longer wave-lengths of the ultraviolet. Servigne, M., and Vassy, E., *Rev. optique*, **16**, 423 (1937); *Chem. Abs.*, **32**, 6154 (1938).

[2] Masson, M. A., *Ann. chim. phys.*, **31**, 295 (1851).

[3] Wilsing, J., *Astrophys. J.*, **10**, 113 (1899).

[4] Baly, E. C. C., "Spectroscopy," II, 128, London, Longmans, Green (1927).

Among the first to employ the continuous spectrum emitted under water as a source for the study of the fine structure of absorption bands were Henri and de Laszlo.[5] Two condensers, each of 2.3×10^{-3} microfarad capacity, were connected in parallel and charged by a transformer supplied with a primary current of 20 amperes at 60 volts, interrupted 600 times a second. There was an auxiliary air spark gap of 15-20 millimeters and an underwater spark between rods of aluminum or copper. The spark was placed 5 centimeters below the surface and at a distance of 10-15 millimeters from a quartz window. The frequency of the oscillatory discharge was found to be of the order of one million per second. The spark was fairly uniform. An exposure of three to five minutes gave a continuous spectrum extending as far as 2100A.

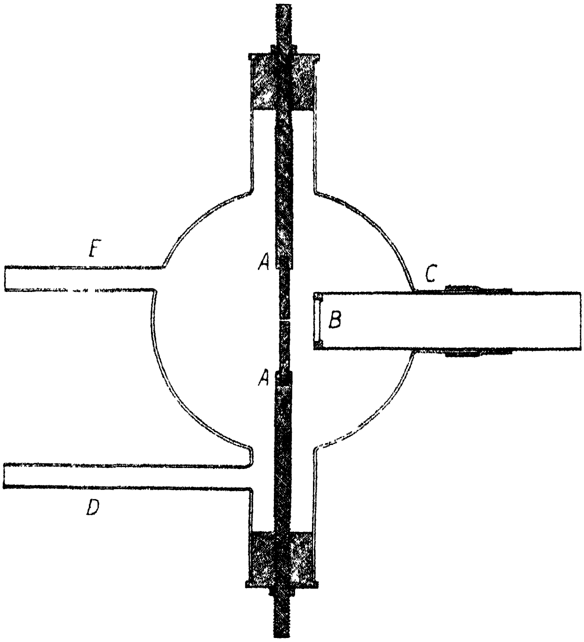

FIGURE 78.

Howe [6] and later Strachan [7] used brass electrodes, with 4 to 6 kw. in the primary of the transformer and secured a very satisfactory continuous spectrum extending to 2200A. Fulweiler and Barnes [8] omitted the Tesla coil and employed the arrangement shown in Figure 78.

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[5] Henri, V., and de Laszlo, H. G., *Proc. Roy. Soc.*, **105A**, 668 (1924).

[6] Howe, H. E., *Phys. Rev.*, **8**, 674 (1916).

[7] Strachan, E. K., unpublished communication to Fulweiler, W. H., and Barnes, J., *J. Frank. Inst.*, **194**, 84 (1922).

[8] Fulweiler, W. H., and Barnes, J., *J. Frank. Inst.*, **194**, 83 (1922).

The electrodes A consisted of tungsten rods 3.5 mm. in diameter. These were mounted in brass rods which screwed into solid rubber stoppers. The stoppers were sealed with hard wax on the side tubes of a "Pyrex" glass bulb of about 500 cc. capacity. By means of the threads on the brass rods the position of the spark gap relative to the quartz window B, and also the length of the gap could be easily adjusted. Fulweiler and Barnes found under the electrical conditions used that a spark length of about 0.5 mm. was the most satisfactory. The quartz plate B, 16.5 mm. diameter, was fixed by washers and screw cap to the end of a brass tube which slipped through the side tube C of the vessel and was held in position by a rubber tube. The spark gap was about 1 cm. from the window and about 2 cm. below the surface of the water which flowed in through the tube D and out at E. For the production of the spark, Fulweiler and Barnes employed a G.E. x-ray transformer, type K, using 15 amperes from the 110 volt a.c. mains on the primary coil. A mercury interrupter which made and broke a d.c. current about 120 times a second was also employed. For capacity, two Leyden jars of about 0.001 mfd. each were used. A zinc spark gap upon which a blast of air was directed was placed in series with the tungsten spark. Figure 79 shows this electrical circuit where T is the transformer; C, the capacity; S, the external spark gap and W, the tungsten spark. The choice of tungsten for the electrodes was made after a careful trial of aluminum, brass, iron, nickel, carbon, tungsten and molybdenum. The tungsten gave more rays in the shorter wave-lengths and required very much less adjustment. Using 1.6

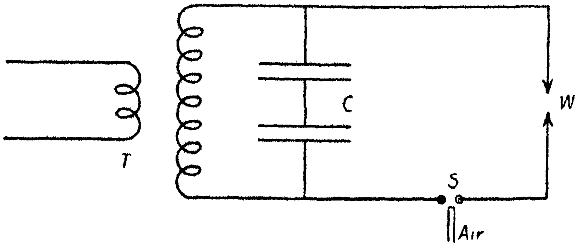

FIGURE 79.

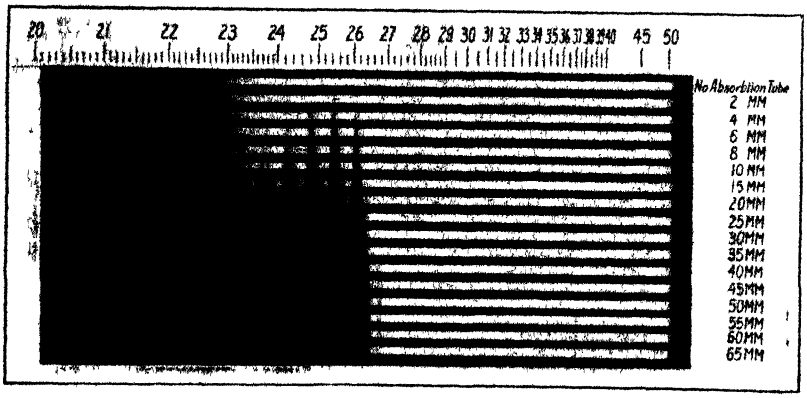

FIGURE 80.

kilowatts in the primary of the transformer, the tungsten electrodes disintegrated very slowly compared with aluminum poles used under exactly the same conditions. Figure 80 illustrates the continuity of the spectrum thus obtained. The absorption bands are those of a 0.1-per cent solution of benzene in ethyl alcohol. The lengths of the solution used are indicated on the side of the plate. This photograph was taken with a Hilger quartz spectrograph. The top exposure with no absorption tube indicates the uniformity of the irradiation. In the original negative the spectrum extends to 2050A.

Snyder [9] employed a Tesla spark maintained under water, and utilized especially designed holders for the electrodes. Allin [10] found the uranium spark under water to give a perfectly continuous, intense spectrum with neither absorption nor emission lines. McNicholas [11] employs spark terminals of tungsten (with about a 16 millimeter gap) enclosed in an ebonite box through which a stream of distilled water is circulated. The adjustment and centering of the spark is accomplished by external controls. Lewis [12] has compared ductile uranium, tungsten-steel and aluminum as electrode materials for the underwater spark.[13]

The theory of the continuous nature of the underwater spark in relation to black body radiation has awakened some interest. Wilson [14] has calculated from the position of the intensity maximum of the OH absorption bands in some spark spectra that the effective temperature of the underwater spark is 5115°. Wyneken [15] determined the energy distribution of the underwater spark between aluminum electrodes by photographic-photometric comparison with the known energy distribution of the carbon arc. A definite maximum occurs at 2850A, (with aluminum electrodes) where the intensity is approximately three and one-half times as great as it is in the neighborhood of 4500A. The position of the maximum would indicate, if the radiation were purely thermal, a temperature of 10,000°K. The experimental curve was, however, much steeper than the theoretical black-body radiation curve for this temperature. Substitution of copper electrodes gave no indication that the curve depends on the electrode material. The falling off of the curve in the extreme ultraviolet was not regarded as due to absorption by the water. Very similar results were reported by Wrede.[16] An increase in the energy of the discharge displaces the maximum intensity towards shorter wave-lengths in conformity, in the case of zinc, with Wien's law for temperature radiation. For smaller discharge energy, the temperature of the spark was calculated to be of the order of 7500°K. and for greater energy 10,000°K. In the case of aluminum and magnesium the shift with increasing energy of discharge was less marked than with zinc, cadmium, copper, lead or tin. The temperatures so determined refer to the inner part of the spark, while the much lower temperature found by Wilson probably refers to the mantle surrounding the spark, since his determination was made by calculation from the maximum absorption of a band spectrum. By this method, Stücklen [17] calculated the temperature of the absorbing OH mantle around the underwater copper spark to be 3000°Abs.

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[9] Snyder, V. D., *J. Am. Chem. Soc.*, **49**, 2510 (1927).

[10] Allin, E. J , *Trans. Roy. Soc. Canada*, **21**, Section 3, 231 (1927).

[11] McNicholas, H. J., *Bureau Standards J. Research*, **1**, 939 (1928). Details of construction also are given.

[12] Lewis, S. J., *Chemistry and Industry*, 464, 1933.

[13] See also Tyndall, E. P. T., *Bureau Standards Tech. Paper, 148* (1920), appendix

[14] Wilson, E. D., *J. Opt. Soc. Am.*, **17**, 37 (1928).

[15] Wyneken, I., *Ann. Physik*, **86**, 1071 (1928)

[16] Wrede, B., *Ann. Physik*, **3**, 823 (1929).

[17] Stücklen, H., *Naturwiss.*, **18**, 248 (1930).

Incandescent Sources. Cohn and Andresen-Kraft[18] suggested as a continuous source for absorption work, the light from cathode-ray bombardment (either in a gas or high vacuum) of a thorium-layered anode. The spectrum was said to extend from 2200 to 6000A, with a maximum intensity at 4500A. Weingeroff,[19] however, did not believe this source to meet the requirements of a truly continuous spectrum. De Kowalski[20] and later Gelhoff[21] used tungsten lamps at 20 to 30 per cent over-rating. (See Chapter 3.) This method gives a continuous but somewhat expensive source, as the lamps burn out quickly. In lamps intended for such use,[22] the filament may be put half as close as usual to the wall, a portion of the latter being of quartz. Weingeroff described a source in which a tungsten cylinder in vacuum, nitrogen or a noble gas is made to glow by an electric current. The Osram Co. produce a tungsten lamp in Uviol glass which operates at 250 volts and 2 amperes, and transmits a continuous spectrum to 2900A.

Hydrogen Discharge Tube. The continuous molecular hydrogen spectrum was first observed by Dove,[23] according to Chalonge and Zé.[24] Freeman has traced the history of work on this phenomenon.[25] It was shown by Horton and Davies[26] that slow-moving electrons in hydrogen produce a continuous spectrum. Lemon,[27] using a discharge tube with a Wehnelt cathode, found that by varying the filament temperature, he could get in succession, and almost pure, Balmer lines, the molecular spectrum of hydrogen and the continuous spectrum.[28] Carst[29] concluded, as did Horton and Davies, that the hydrogen molecule is the carrier of the spectrum, which is distinct from the continuous spectrum which is to be expected at the series limit. The use of the hydrogen discharge tube as a source of continuous ultraviolet radiation was introduced by Tingey and Gerke.[30] Their source, however, lacked intensity, and exposures of at least an hour often were necessary.

Gehrcke and Lau[31] described the structureless nature of radiations emitted between 3300 and 1950A by pure hydrogen in an alternating current discharge in an inside silvered tube. Bonhoeffer and Steiner[32] employed this source in the absorption spectrophotometry of hydrogen iodide.

A great impetus to the more general use of the hydrogen discharge came from the work of Bay and Steiner,[33] who increased the intensity by employing an end-on arrangement. Also the current density was made as high as possible by loading the tube heavily. They employed aluminum electrodes extending close to the walls, the electrodes having areas of 300 square centimeters. It was stated that the electrodes could carry as much as 500 milliamperes for a day. To get the current density high, the luminous portion of the tube was constricted. One of their tubes was water-cooled at the constriction. The tube (Figure 81) consisted of an ordinary glass tube (L) 60 centimeters long and 5 millimeters in diameter X, two electrode vessels (G), one of which has a tube (R) carrying a quartz or fluorite window and the other a 5-liter bulb (V). The apparatus was supported with the lower luminous tube in a bath with flowing water. The tube was filled with hydrogen at 1-2 millimeters pressure and sealed. Failures of these tubes led them to develop a tube that would operate under loads up to 500 or even 700 milliamperes,[34] which is important since the ultraviolet emission increases with the current density. The ratio of ultraviolet emission to the radiations in the visible range increases with the hydrogen pressure. For the continuous radiation from the hydrogen lamp, the ratio is 6:1, while that of the mercury lamp is only 0.6:1. Bay and Steiner [35] also made use of an electrodeless oscillating discharge in well-dried hydrogen.

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[18] Cohn, W. M., and Andresen-Kraft, C., *Z. tech. Physik*, **12**, 428 (1931); *J. Am. Ceram. Soc.*, **15**, 122 (1933).

[19] Weingeroff, M. A., *Physik. Z. Sowj.*, **2**, 278 (1932).

[20] de Kowalski, J., *Arch. des Sciences*, **37**, 265 (1914).

[21] Gelhoff, G., *Z. tech. Physik*, **1**, 224 (1920).

[22] British P. 359,712, October 29, 1931, to N. V. Philips' Gloeilampenfabrieken.

[23] Dove, *Pogg. Ann.*, **104**, 186 (1858).

[24] Chalonge, D., and Zé, N. T., *J. Phys. Radium (7)*, **1**, 416 (1930).

[25] Freeman, I. M., *Astrophys. J.*, **64**, 122 (1926).

[26] Horton, F., and Davies, A. C., *Phil. Mag.*, **46**, 892 (1923).

[27] Lemon, H. B., *Nature*, **113**, 127 (1924).

[28] See also Richardson, O. W., and Tanaka, T., *Proc. Roy. Soc.*, **106A**, 640 (1924).

[29] Carst, A., *Ann. Physik*, **75**, 665 (1924).

[30] Tingey, H. C., and Gerke, R. H., *J. Am. Chem. Soc.*, **48**, 1838 (1926); see also Bates, J. R., and Taylor, H. S., *Ibid.*, **49**, 2441 (1927).

[31] Gehrcke, E., and Lau, E., *Ann. Physik*, **76**, 673 (1925).

[32] Bonhoeffer, K. F., and Steiner, W., *Z. physik. Chem.*, **122**, 287 (1926).

[33] Bay, Z., and Steiner, W., *Z. Physik*, **45**, 337 (1927).

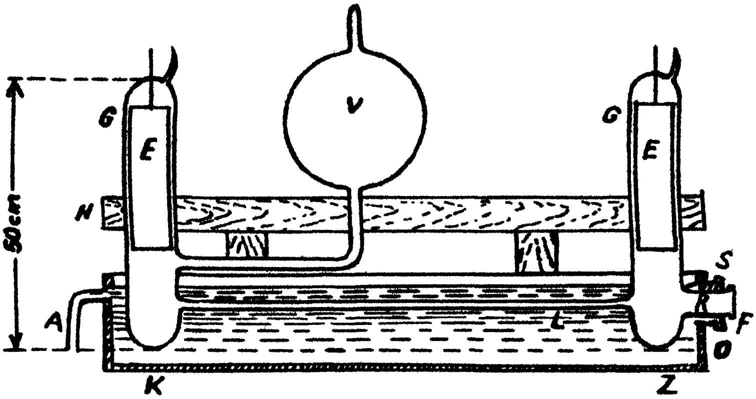

FIGURE 81. Hydrogen Discharge Tube of Bay and Steiner *(Zeitschrift für Physik).*

Another development of the discharge tube was made by Lambrey and Chalonge,[36] who used only 15-30 milliamperes to operate the tube for five minutes They [37] extended their work to include tubes with both interior electrodes and tubes with only exterior electrodes operating at 500,000 cycles. They found that as the pressure increases, the intensity of the continuous spectrum passes through a maximum at a hydrogen pressure of 2-3 mm. For a given pressure, the intensity increases with the current, but the energy distribution is not modified. As compared with a carbon arc, the intensity is about 2.1 times as great at 4400A and 23 times as great at 2200A.[38]

Considerably greater currents were carried in a tube devised by Lawrence and Edlefsen.[39] The electrodes were aluminum cylinders 6 centimeters in diameter and 40 centimeters long, open at the bottom and closed at the top, and attached to tungsten leads passing through "Pyrex" containing tubes. The bottom edges of electrodes were rounded off and made close-fitting to the containing tubes for cooling by conduction. The two large "Pyrex" tubes containing the electrodes were joined through a tube of quartz 7 millimeters in diameter and 60 centimeters long. The connecting tube was sealed to the confining tubes by a water-cooled wax joint. The tube was insealed into short quartz tubes of larger diameter at each end and the larger quartz tubes were waxed to "Pyrex" side tubes. Two inflow jets of water flowed in the region between the small and large quartz tubes and kept the wax joints cool despite the great generation of heat nearby. The whole tube was immersed in a tank of water to the dotted line (Figure 82). This cooling was adequate for 6.5 amperes at 3000 volts, but the tube was ordinarily run at 3 amperes. There was some unsteadiness and bumping at the middle of the connecting tube unless additional water jets were provided along the quartz tube. The tube was used end-on, through a quartz window W waxed on a "Pyrex" side tube through the tank wall.

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[34] Bay, Z., and Steiner, W., *Z. Physik,* 59, 48 (1929).
[35] Bay, Z., and Steiner, W., *Z. Elcktrochem.,* 34, 657 (1928).
[36] Lambrey, M., and Chalonge, D., *Compt. rend.,* 184, 1057 (1927).
[37] Lambrey, M., and Chalonge, D., *Compt. rend.,* 188, 1104 (1929).
[38] See also Chalonge, D., and Zé, N. T., *Compt. rend.,* 190, 632 (1930); Chalonge, D., *Z. Astrophys.,* 15, 82 (1938).
[39] Lawrence, E. O., and Edlefsen, N. E., *Rev. Sci. Instruments,* 1, 45 (1930).

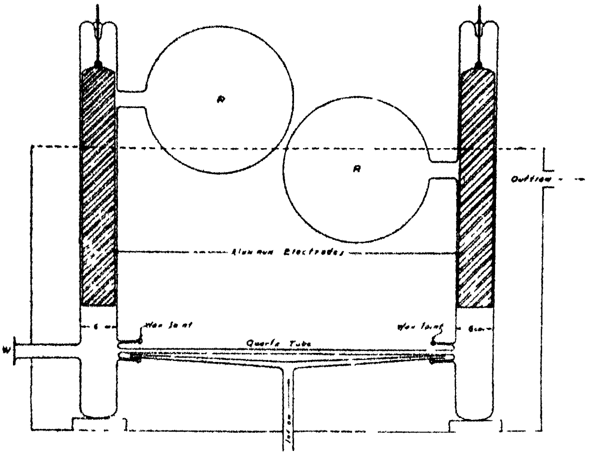

FIGURE 82. Water-cooled Hydrogen Discharge Tube of Great Carrying Capacity (Lawrence and Edlefson, *Review of Scientific Instruments*).

It was only necessary to evacuate the tube by an oil pump to 0.01 millimeter and flush it several times with commercial tank hydrogen. The pressure was not very critical, and the hydrogen pressure was merely reduced to allow a discharge of several amperes to pass at 3000 volts. Lines appeared at first but after several hours to a day of operation, the lines due to impurities disappeared and the region from 3000 to 2000A became continuous. Two large flasks (R) served as hydrogen reservoirs. The tube could be operated steadily over long periods. Data obtained by the aid of a monochromator and thermopile indicated that the intensity of the ultraviolet does not vary greatly from the near ultraviolet to 2000A. The intensity at 2536A seemed of the same order as that obtained from a Cooper-Hewitt lamp at ordinary currents. The tube yielded about ten times the intensity of the first Bay and Steiner tubes, and was much more intense than the usual ultraviolet available for spectroscopy, exposures of 0.1 second being adequate.

Other tubes were described by Kistiakowsky[40] and by Urey, Murphy and

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[40] Kistiakowsky, G. B., *Rev. Sci. Instruments*, 2, 549 (1931).

Duncan.[41] The latter tube, of glass, was very compact and so well cooled that currents up to 2 amperes could be carried for long exposures without breakage. One end only is indicated in Figure 83; the other is identical. The tube was composed of "Pyrex" with crystal quartz windows stuck on each end with de Khotinsky cement. The electrodes D were cylinders of sheet aluminum, the edges of which were spot welded. They were joined to the tungsten lead A by German silver wire. The electrodes were held by glass prongs. A rapid stream of water flowed into B and after circulating around the inner tube flowed out again at the other end. Two small cooling jackets were placed near the windows to prevent the wax from getting warm, but they did not seem necessary. The inner tube through which the discharge passed was moistened with silver nitrate solution which was readily reduced to silver by the discharge. The tube was evacuated at C and in the same position at the other end a palladium tube was connected by a soft glass-to-"Pyrex" graded seal. Hydrogen was admitted through the palladium by heating the latter with a small hydrogen flame. The discharge was run repeatedly with the addition of hydrogen and evacuation until the spectrum seemed satisfactory, as viewed with a direct-vision spectroscope. The tube was sealed off from the pumping system at C. As the hydrogen gradually cleaned up, more could easily be added at the palladium tube. A 5-kv. autoregulating transformer supplied the high potential. With 110 volts and about 50 amperes on the primary, it gave 2500 volts on the secondary. An ammeter in series with the tube showed 2 amperes under the best operating conditions. A fan was directed on the outside of the tube as a further aid to

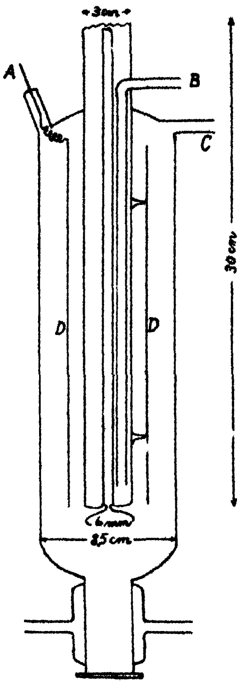

FIGURE 83.

Hydrogen Discharge Tube of Urey, Murphy, and Duncan *(Review of Scientific Instruments).*

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[41] Urey, H. C., Murphy, G. M., and Duncan, J. A., *Rev. Sci. Instruments*, 3, 497 (1932)

cooling. Even after long exposures, the tube remained quite cool, and was satisfactory after a year of use. Employed with the Hilger E1 spectrograph, it was possible to obtain certain bands of nitric oxide at 2050 and 2150A in absorption with exposures of one to five minutes, using Eastman U. V. Spectroscopic Plates. Dawson[42] described a tube for discharge in hydrogen at 30 to 100 millimeters pressure. The tube could be viewed side-on through a constricted quartz tube joining two hollow electrodes in glass supporting tubes.[43]

According to Henry, the hydrogen discharge tube has become the most suitable and probably also the most used continuous source.[44] Most such tubes give intensities which are too weak. Henry modified somewhat the disposition of the electrodes and employed hydrogen at a pressure of 4 millimeters. He used 1200 volts at the electrodes and usually 2 amperes, although this could be raised to 3.5 to 4 amperes.

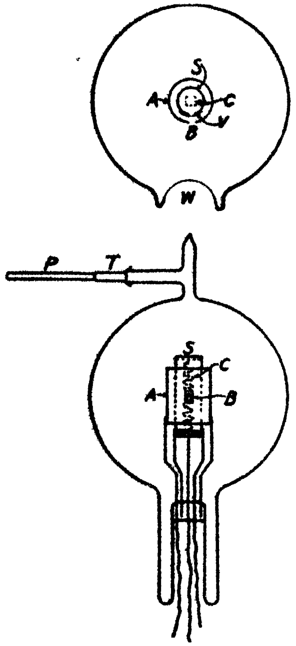

FIGURE 84.

Hydrogen Discharge Tube of Munch *(Journal American Chemical Society).*

Munch[45] states that the hydrogen continuum may be excited at about 5 per cent of the voltage required by other discharge tubes and without water cooling, by means of thermoelectrons from a hot cathode. For example, the low voltage arc of Duffendack and Manley[46] may be utilized. This arc passed between a heated tungsten filament and a disk anode, in a tube containing a palladium tube to admit hydrogen and a quartz window sealed on with wax. Munch modified this tube by employing an oxide-coated cathode (C in Figure 84). This cathode is a 0.48 × 15.25 centimeter piece of nickel gauze bent into a corrugated form having a 0.48 centimeter cross-section, suspended between a cathode shield of nickel and a nickel wire and coated with barium and strontium carbonates. The cylindrical cathode shield, S, of 0.125 millimeter nickel, 4.06 centimeters long and 1.25 centimeters in diameter, forms one lead to the cathode and is closed at the bottom by means of a porcelain disk through which the second cathode lead passes. The only opening in the shield is a 0.66 × 3 millimeter slit cut in a piece of 0.25 millimeter sheet tungsten welded in the side. The surrounding anode (A) is a 2.2 × 2.86 centimeter nickel cylinder with a hole (B) to correspond to the slit in the cathode shield. The electrodes are mounted on a five-wire stem and sealed into a 10-centimeter "Pyrex" bulb. A thin window (W) is made opposite the slits by blowing a bubble about 3.2 centimeters in diameter, melting it back to about half its height and sucking it in carefully. The palladium tube (P) is silver soldered to a copper tube (T) the end of which is flared and sealed on the outside of a piece of Nonex which is fused to the "Pyrex" from which the bulb is made. The tube is evacuated and freed of all traces of moisture or carbon monoxide. The glass and metal parts are outgassed by passing a discharge through the tube and sweeping it out with a stream of hydrogen at 2-4 millimeters pressure. The hydrogen is admitted by holding a Bunsen burner under the palladium tube. When the spectrum becomes continuous below 3657A, the tube is sealed off. The cathode requires 9 amperes at about 3 volts, supplied by a step-down transformer and connected in series with a rheostat and ammeter. The anode circuit, also containing a rheostat and ammeter, may be connected to any 110-volt circuit. In operation, the potential drop between anode and cathode is 30-35 volts. The whole discharge between the cathode and anode must pass through the small slit in the shield and is viewed through the opening in the anode. It can operate continuously at a current of 1.5 ampere, the current density being 75 amperes per square centimeter. This may be increased considerably for short periods. In comparison with the intensity of the mercury lines of a "Labarre," both sources being run at 1 ampere, the continuum was 25 per cent as intense as the 2483 and 2652A lines, 7 per cent as intense as the 2894 and 3022A lines and 12 per cent as intense as the 3350A lines.

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[42] Dawson, L. H., U. S. P. 1,922,281, Aug. 15, 1933; *Chem. Abs.*, **27**, 5006 (1933).

[43] See also Stevens, D. S., *Rev. Sci. Instruments*, **6**, 40 (1935).

[44] Henry, L., *J. chim. phys.*, **31**, 665 (1934).

[45] Munch, R. H., *J. Am. Chem. Soc.*, **57**, 1863 (1935).

[46] Duffendack, O. S., and Manley, J. H., *J. Opt. Soc. Am.*, **24**, 222 (1934).

Other descriptions of tubes for this purpose were made by Watson and Hurst,[47] Almasy and Kortüm,[48] Jacoby,[49] and Smith.[50] Hydrogen discharge tubes carrying up to 1 ampere have been prepared by the Hanovia Co.

According to the Hilger Co., the distribution of radiation from hydrogen discharge tubes is so far from uniform that the tubes cannot be used for measurements of density with their "Spekker" photometer. Furthermore, when run on alternating current, the intensity of radiation increases to a maximum and dies away to zero once in each half-phase of the applied alternating current, so that it cannot be assumed that for any speed at which the use of a sector fulfills the reciprocity law, the effective density of the sector can be derived from its aperture. To overcome this, a rocking quartz tube has been made available. Its speed of oscillation is such that the energy received by the apertures of the "Spekker" photometer is uniform over that area, in a vertical plane, for all exposures over twenty seconds.

Smith and Fowler[51] have described a 220-volt d.c. discharge tube which can be operated with currents as high as 20 amperes to give an intense ultraviolet continuum. (Figure 85). The cathode of 25 cm. of 40 mil tungsten wire was attached to the water-cooled cathode leads of copper tubing by set screws. The leads were attached to the "Pyrex" cathode section (C) by copper-to-"Pyrex" seals (F). The filament current (50-60 amperes) was supplied by a 220 to 30-volt transformer. The discharge tube (A) was of 7 mm. inside diameter quartz tubing attached to a 100 cc. quartz flask, which was sealed with picein to a water-cooled metal ring (B). This metal ring in turn was sealed with picein to the cathode section (C). The anode consisted of a hollow copper male joint (D), sealed with picein to a No. 50 Pyrex joint (E), the anode chamber. The latter was attached to the quartz discharge tube by means of a water-cooled picein seal. A quartz window was sealed to the far end of the hollow anode. For a given potential across the tube, the pressure for greatest intensity of the continuum was not very critical, but it varied greatly with the voltage. Pressures of 0.20 to 0.27 mm. were usually employed with potentials of 220 volts.

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[47] Watson, W. H., and Hurst, D. G., *Can. J. Research,* **13A,** 19 (1935).

[48] Almasy, F., and Kortüm, G., *Z. Elektrochem.,* **42,** 607 (1936).

[49] Jacoby, G., *Z. tech. Physik,* **17,** 382 (1936); *Physik. Z.* **37,** 808 (1936).

[50] Smith, N. D., *J. Opt. Soc. Am.,* **32,** 2832 (1938). This tube uses a 5.3 cm. capillary of rectangular cross-section 1.3 × 6 mm., with a gas pressure of 1-2 mm.

[51] Smith, A. E., and Fowler, R. D., *J. Opt. Soc. Am.,* **26,** 79 (1936).

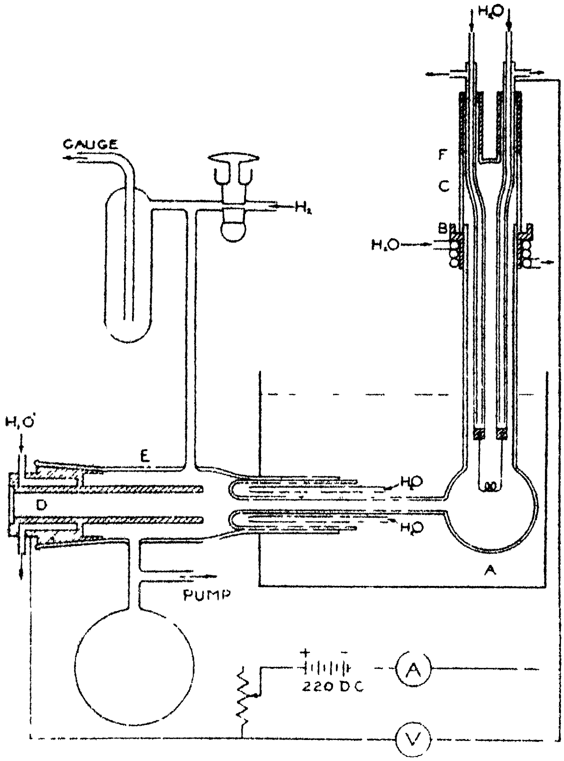

FIGURE 85. Hydrogen Discharge Tube of Smith and Fowler *(Journal Optical Society of America).*

THEORY OF THE CONTINUOUS SPECTRA OF HYDROGEN

To discuss the many investigations directed toward an understanding of the theory of the origin of the continuous spectrum which extends from the visible to the Schumann region would lead us far beyond the scope of this book. A thorough discussion of the origin of the continuous spectra of gases, with 323 references, has been given by Finkelnburg.[52] Chalonge and Zé [53] have reviewed in detail the work relating to the hydrogen spectrum. Beyond the Balmer lines there lies (as discussed in Chapter 2) a continuous spectrum related to the excitation of the hydrogen atom beyond its ionization potential, as explained by Bohr.[54] In the discharge tube, the Balmer lines are widened by the Stark effect and the related continuous spectrum is displaced toward the red. Chalonge and Zé [55] have found evidence also for the existence of another continuous spectrum similarly related to the Paschen series of lines and extending into the infrared.

These continuous spectra are not, however, very significant in the radiations emitted by the tubes described in the preceding section. The effective continuous spectrum is related to the hydrogen molecule, which itself produces a "secondary," many-lined, or band, spectrum, regarding which there is a vast literature. One of the earliest theories relating the hydrogen molecule to the continuous spectrum produced in these sources assumed the spectrum to be due to dissociation of the hydrogen molecules into atoms possessing various kinetic energies, the radiations being emitted during their recombination.[56]

Discrepancies in regard to the relation between the heat of dissociation of the hydrogen molecule and the long wave-length limit of the continuum led to a number of suggestions in which variously excited, rather than resting state, molecules were regarded as dissociating.[57]

More recently, efforts have been directed toward the examination of the potential energy curves for the atoms of the hydrogen molecule from the standpoint of the wave-mechanics, the general features of which in relation to photochemistry are discussed in Chapter 13. For the reader desiring to study the application of these theoretical developments to the hydrogen continuum a few significant papers are cited.[58]

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[52] Finkelnburg, W., *Physik. Z.*, **31**, 1 (1930).

[53] Chalonge, D., and Zé, N. T., *J. Phys. Radium,* (7) **1**, 416 (1930).

[54] Bohr, N., *Phil. Mag.*, **26**, 17 (1913).

[55] Chalonge, D., and Zé, N. T., *Compt. rend.*, **189**, 243 (1929); **190**, 425 (1930).

[56] Schüler, H., and Wolf, K. L., *Z. Physik*, **33**, 42 (1925).

[57] Takahashi, Y., *Japan. J. Phys.*, **4**, 103 (1927); *Chem. Abs.*, **21**, 3829 (1927). Takahashi, Y. and Fukumoto, Y., *Sci. Repts. Tohôku Imp. Univ.*, **17**, 675, 963 (1928); *Chem. Abs.*, **23**, 3834 (1929). Freeman, I., *Astrophys. J.*, **64**, 122 (1926). Oldenberg, O., *Z. Physik*, **41**, 1 (1927). Herzberg, G., *Physik. Z.*, **28**, 727 (1927). Jezewski, H., *Compt. rend. soc. polonaise phys.*, **3**, 161 (1927); *Chem. Abs.*, **23**, 5106 (1929). Newman, *Phil. Mag.*, **6**, 807 (1928). Kaplan, J., *Proc. Nat. Acad. Sci.*, **13**, 760 (1927). Winans, J. G., and Stueckelberg, E C. G., *Ibid.*, **14**, 867 (1928); Franck, J., and Jordan, P., "Anregung von Quantensprungen durch Stösse," p. 261, Berlin, J. Springer, **1927**.

[58] Heitler, W., and London, F., *Z. Physik,* **44**, 455 (1927). Sugiura, Y., *Z. Physik,* **45**, 484 (1927); *J. Phys. Radium,* **8**, 113 (1927). Birge, R., *Proc. Nat. Acad. Sci.*, **13**, 462 (1927). Condon, E. U., *Phys. Rev.*, **28**, 1182 (1926); *Proc. Nat. Acad. Sci.*, **13**, 462 (1927). Franck, J., *Trans. Faraday Soc.*, **21**, part 3, (1925). Epstein, P. S., and Muskat, M., *Proc. Nat. Acad. Sci.*, **15**, 405 (1929). Goldstein, L., *Compt. rend.*, **193**, 485 (1931). Smith, A. E. and Fowler, R. D., *J. Opt. Soc. Am.*, **26**, 79 (1936); McDonald, J. K. L., *Proc. Roy. Soc.*, **A 136**, 528 (1932). Finkelnburg, W., and Weizel, W., *Z. Physik,* **68**, 577 (1931).

Chapter 10

Protective Glasses, Ultraviolet-Transmitting Glasses and Filters

The ability of glasses of various compositions to absorb or transmit ultraviolet or other radiations is of importance when viewed from either of two opposite aspects. It may be desired on the one hand to develop a glass capable of protecting the eyes of a worker from injurious radiations, or, on the other, it may be desired to produce a glass which transmits the solar ultraviolet more completely than ordinary window glass.[1] Mention of protective glasses is made here to remind the experimentalist not to disregard suitable protection for the eyes when working with ultraviolet rays.

Protective Glasses

Exposure to rays emitted in electric welding and in the employment of the oxy-acetylene torch for cutting and welding steel has been the cause of many cases of inflammation of the eyes. In arc welding, the eyes require protection from intense visible light or glare, from intense infrared or heat rays and from ultraviolet radiations. Andrews[2] affirms that the ultraviolet rays are the most dangerous because they are not only invisible but also because we are unprovided by nature with any organ or sense for detecting them. Furthermore, it should be noted that the harmful effects are not immediately produced but become evident only some time after the exposure. Fortunately, the most deleterious of the ultraviolet rays are absorbed by a moderate thickness of ordinary glass.

The symptoms of conjunctivitis caused by intense light or by ultraviolet rays are abnormal intolerance to light, excessive secretion of tears, intense smarting of the lids, contraction of the pupils, sometimes swelling of the lids, and more rarely, small ulcers developing on the eyeball or cornea. Fortunately, the lesions are usually superficial, because the cornea absorbs all radiations below 3000A and the lens those below 3500A, thereby protecting the retina. However, unless properly treated by a physician, infection may occur, resulting in chronic inflammation of the conjunctiva, cornea, iris or retina and possibly blindness. Under proper treatment, most cases recover in a few days.

In 1914, Crookes[3] investigated over 300 specimens of glass in an endeavor to find a colorless glass which would absorb all the ultraviolet and infrared rays. Although he did not find a colorless glass which met this specification, he developed a blue-green glass which absorbed about 90 per cent of the radiant heat and which was opaque to ultraviolet rays. The glass was sufficiently free from color to be scarcely noticeable when used as spectacles. The ideal glass which will transmit all the colors of the spectrum, cutting off the invisible rays at each end, has still to be discovered.

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[1] Chance, W. H. S., and Hampton, W. M., [*Proc. Optical Convention*, **1926**, 1, 24; *Chem Abs.*, **21**, 3111 (1927)], reviewed the early manufacture of the filtering glasses produced by Chance Bros. & Co., Ltd. Methods of measuring the transmission of ultraviolet rays by glasses were discussed by Shapiro, C. V., *Am. J. Physiol.*, **87**, 396 (1928), and Schachtschabel, K., *Ann. Physik*, **81**, **929** (1926).

[2] Andrews, W. S., *Gen. Electric Rev.*, **9**, 303 (1917).

[3] Crookes, W., *Trans. Roy. Soc.*, **214**, 1 (1914).

Luckiesh,[4] Gage[5] and Martin[6] have given data on the transmission of the earlier commercial protective glasses. The latter also have been studied at the Bureau of Standards.[7]

A number of commercial glasses, including 82 examined by Gibson and McNicholas, were investigated. Crookes A, Corning 91B, American Optical Co. Nos. 57 and 58, and Noviol O were most efficient in protecting against ultraviolet rays. The latter two, the most efficient, were not nearly so colorless as the other three. A combination of Noviol A and Corning 124J absorbs all the ultraviolet and most of the infrared and, although light green, still has a high visible transmission.[8] The Bureau developed a blue glass for furnace workers by replacing half the lime in a soft soda-lime glass with cerium oxide to stop the ultraviolet and adding sufficient cobalt oxide to produce the blue color desired by workmen. The glass registered 20 + 8 on the Lovibond scale.[9] The glass may contain SiO_2 60-80, CaO 0-12, CeO 5-10, CoO 0.1-0.5 and Na_2O 12-25 percent.[10] A thin film of gold[11] absorbs infrared and ultraviolet and to some extent visible rays, depending upon the density of the film.[12] Inagaki reported Noviweld and certain Crookes glasses suitable for specified uses in glass plants.[13] Coblentz and Stair[14] have published transmission curves of optical crown glass, and several commercial protective glasses. See Figure 86.[14a] Average samples of colorless, vitreous silica were much more opaque than was quartz to radiation shorter than 2400A. A formula for specifying the shade number of protective glasses, based upon experimental tests, was given, together with a table of transmissions and tolerances, corresponding to shade numbers, as proposed by a Federal specification committee. The specifications were somewhat revised in 1930.[15]

A glass advocated by the Corning Glass Works[16] for absorbing ultraviolet radiations is made by adding to an ordinary lime, barium, lead, or zinc glass batch; (A) at least 6 per cent of titanium dioxide, and oxidizing salt (nitre) in sufficient quantity to prevent the reduction of the titanium dioxide, with or without cerium oxide or vanadium oxide; or (B) at least 1 per cent of an oxide of vanadium higher than V_2O_5, with or without an oxidizing agent and a complementary, but absorptively inert substance (manganese dioxide, cobalt, nickel or uranium oxide) to change the hue of the glass from green to amber. Titanium dioxide is about half as effective as cerium oxide. A lime-soda glass containing 7.7 per cent titanium dioxide and 7.7 per cent cerium nitrate is a brilliant clear yellow, and in plates two mm. thick completely cuts off the 3650A line. A glass containing both cerium nitrate and titanium dioxide has a more brilliant color and greater desirable absorption than a glass containing one of these substances superimposed on a glass containing the other. The addition of borax increases the refractive index of the glasses containing titanium dioxide. A large percentage of borax in a glass containing vanadium oxide completely cuts off the ultraviolet 3650A line in plates of 4 mm. thickness. If 2 per cent of vanadium oxide be used, the same cut-off is effected by plates 2 mm. thick.

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[4] Luckiesh, M., *Trans. Ill. Eng Soc.*, **9**, 472 (1914).

[5] Gage, H. P., *Ibid.*, **11**, 1050 (1916); **25**, 337 (1930).

[6] Martin, L. C., *Trans. Opt. Soc*, **18**, April (1917).

[7] Coblentz, W. W, and Emerson, W. B., Tech Paper No. 93 (1917), *Bureau of Standards*, *J. Frank. Inst.*, **183**, 629 (1917); Coblentz, W. W., Emerson, W. B., and Long, M. B., *Bull. Bureau of Standards*, **14**, 663 (1918); *J. Frank. Inst.*, **188**, 255 (1919); Gibson, K. S., and McNicholas, H. J., *Bureau of Standards Tech Paper No 119* (1919); *J. Frank. Inst.*, **187**, 630 (1919). For data on the absorption of cobalt glasses, see Brode, W., *J. Am. Chem. Soc.*, **55**, 939 (1933).

[8] See also Wright, P., *Brit. J. Radiology*, **2**, 434 (1929).

[9] *Ind. Eng. Chem., News Ed*, **3**, No. 24, 6 (1925); Coblentz, W. W., U. S. P. 1,637,439, Aug. 2, 1927; *Chem. Abs.*, **21**, 3114 (1927).

[10] Coblentz, W. W., and Finn, A., *J. Am. Ceram. Soc.*, **9**, 423 (1926); *Brit. Chem. Abs.*, **B**, 667 (1926).

[11] Finely divided gold particles have also been proposed; Warde, F. M. British P. 341,187, Nov. 15, 1929; *Chem. Abs.*, **27**, 2272 (1933).

[12] See Grondall, L. O., *Science*, **70**, 179 (1929). For other metallic films obtained by cathodic sputtering, see Taylor, E. M., Stafford, G., and Rodwell, R. V., and Kapella, Ltd., British P. 479,238, Feb. 2, 1938; *Chem. Abs.*, **32**, 4938 (1938).

[13] Inagaki, T., *Rept. Lab. Asahi Glass Co.*, 1921; *Chem. Abs.*, **16**, 3185 (1922).

[14] Coblentz, W. W., and Stair, R., *U. S. Bureau Standards Tech. Paper* No. 369, 555 (1928).

[14a] The transmissions of several miscellaneous materials, as mother-of-pearl, sextant and signal glasses, heat-transmitting glass, greenish-brown glass, and the organic materials "pollopas" and "protectoid" were also given.

[15] Coblentz, W. W., and Stair, R., *J. Opt. Soc. Am.*, **20**, 624 (1930).

[16] British P. 118,397 and 118,398, April 15, 1918, to Corning Glass Works; *J. Soc. Chem. Ind.*, 584A, 1918. For snow glasses, see also Degea, A.-G., British P. 466,262, May 25, 1937; *Chem. Abs.*, **31**, 8144 (1937).

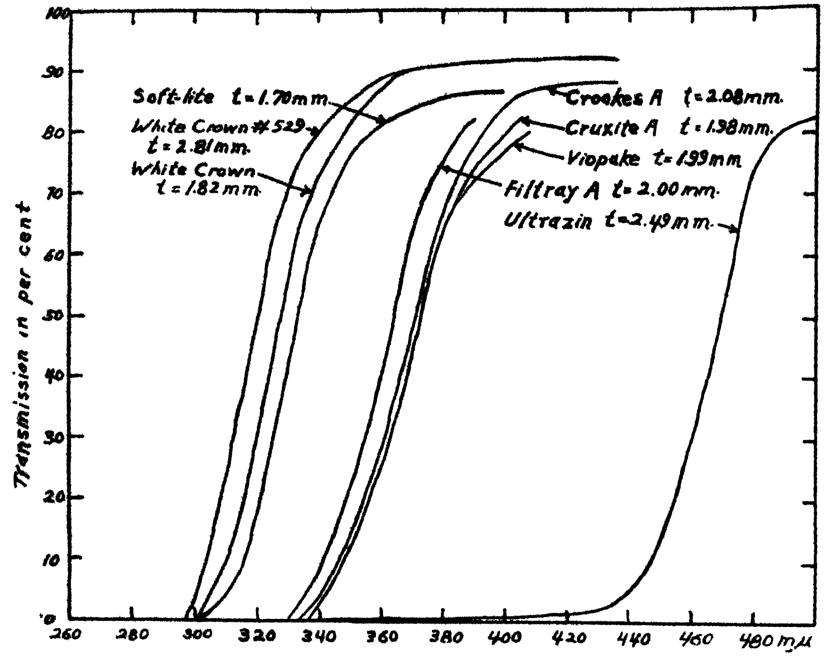

FIGURE 86. Transmission Curves for Various Protective Glasses (Coblentz and Stair, "Bureau of Standards Technical Papers").

Up to 10 per cent of rare earths is used by Deutsche Spiegelglas A.-G.[17] Taylor[18] describes a glass for absorbing ultraviolet rays in which titanium oxide is an essential constitutent. He also[19] obtains a flesh-colored glass of high ultraviolet absorption and good visible transmission by using 3 to 6 per cent cerium dioxide and 0.2 per cent manganese dioxide with silica, potash, soda and lime. In another instance it was proposed to use as the only coloring oxide, 0.2 to 1 per cent of ferric oxide, in making a glass which transmits no ultraviolet, but 84 per cent of the visible, through 2 mm.[20] To absorb both infrared and ultraviolet, not less than 0.3 per cent of cobalt and iron oxides, or 0.5 per cent of As_2O_3 and Sb_2O_3 may be added.[21] Cadmium sulfide and ferrous oxide have also been advocated.[22] A glass, said to be efficient in absorbing ultraviolet rays and practically colorless, is made by Chance Bros.[23] by using two or more ultraviolet-absorbing ingredients, the colors of which neutralize each other. A glass containing approximately 3.3 per cent of cerium and 0.7 per cent of didymium (added as oxides or hydroxides) is said to be practically colorless and efficient in absorbing ultraviolet rays. Another glass transmitting 80 per cent of visible light with but little selective absorption and cutting off all waves shorter than 3800A. contains a small proportion of chromium and vanadium.[24] E. A. Busch A.-G. Optische Ind.[25] colored lenses, regulating the tint as desired, by a suitable glaze, which might be applied only to the upper edge of the glasses, through which it was stated the dangerous rays usually enter the eye. The firm of Zeiss [26] described a glass which greatly weakens rays between 7000 and 15,000A and those below 3600A, while transmitting the visible range. Frank [27] adds to the glass batch a small quantity (0.00256 part by weight) of a mixture of MnO_2, 3 and Fe_2O_3, 2 parts. A thickness of 1.5 mm. absorbs a large proportion of ultraviolet and infrared rays without appreciably reducing the visible. Also, it is stated that laminated glass, with intervening sheets of celluloid or the like, may be made to exclude ultraviolet.[28]

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[17] French P. 720,075, July 16, 1931, to Deutsche Spiegelglas, A.-G.; *Chem. Abs.*, **26**, 3892 (1932).

[18] Taylor, W. C., U. S. P. 1,292,147 and 1,292,148, Jan. 21, 1919; *Chem. Abs.*, **13**, 1005 (1919).

[19] Taylor, W. C., U. S. P. 1,414,715, May 2, 1922; *Chem. Abs.*, **16**, 2206 (1922).

A simple means of evaluating eye-protective glasses was proposed by Bloch.[29] In the ultraviolet (isolated by a "black glass" filter of the Sendlinger Optischer Glaswerke), the transmission of a standard quartz lamp light is estimated from the degree of fluorescence excited on a standard test paper. The results agree well with spectrographic determinations.

Starkie and Turner [30] in transmission studies of sections cut from commercial food containers and ground to 2 mm. thickness, demonstrated a rather definite increase in absorption with rise of the content of ferric oxide. Titanium dioxide also absorbs ultraviolet light, but the amounts found in commercial glasses, usually below 0.02 per cent are too small to function greatly.[31] Translucent sheets of cellulose hydrate are rendered impermeable to ultraviolet rays by treatment with aqueous pine bark extract, according to Gerngross and Callo.[32]

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[20] French P. 760,998, March 7, 1934, to Pittsburgh Plate Glass Co.; *Chem. Abs.*, **28**, 4195 (1934).

[21] German P. 550,782, May 6, 1927, to Deutsche Spiegelglas A.-G.; *Chem. Abs.*, **26**, 4929 (1932).

[22] French P. 752,615, Sept. 27, 1933, to Verreries de Goetzenbruck; *Chem. Abs.*, **28**, 1160 (1934).

[23] Gell, P. V. W., Gould, C. E., Hampton, W. M., and Martin, H. S., U. S. P. 1,634,182, June 28, 1926, to Chance Bros. & Co., Ltd.; British P. 256,737, June 5, 1925; *Brit. Chem. Abs.*, **B**, 878 (1926); *Chem. Abs.*, **21**, 2775 (1927).

[24] Gould, C. E., British P. 316,464, Sept. 8, 1928, to Chance Bros. & Co., Ltd.; *Brit. Chem. Abs.*, **B**, 816 (1929).

[25] German P. 424,811, Jan. 10, 1925, to E. A. Busch, A.-G. Optische Ind.; *Brit. Chem. Abs.*, **B**, 789 (1926).

[26] British P. 252,130, May 16, 1925, to Firm of C. Zeiss Co.; *Chem. Abs.*, **21**, 1528 (1927).

[27] Frank, I., U. S. P. 1,615,448, Jan. 25, 1927; *Brit. Chem. Abs.*, **B**, 365 (1927); Chem. Abs., **21**, 808 (1927).

[28] Murray, G. H., U. S. P. 1,958,013, May 8, 1934; *Chem. Abs.*, **28**, 4196 (1934).

[29] Bloch, L., *Gas und Wasserfach.*, **70**, 1229 (1927); *Chem. Abs.*, **22**, 850 (1928); *Brit. Chem. Abs.*, **B**, 231 (1928). See also Danckwortt, P., and Jürgens, E., *Arch. Pharm.*, **272**, 713 (1934).

[30] Starkie, D., and Turner, W. E. S., *J. Soc. Glass Tech.*, **12**, 27 (1928); *Chem. Abs.*, **22**, 2821 (1928).

[31] Smith, A. W., and Sheard, C., [*J. Opt. Soc. Am.*, **2**, 26 (1919)] gave earlier work on the absorption of ultraviolet light by glasses.

[32] Gerngross, O., and Callo, A., U. S. P. 2,106,599, Jan. 25, 1938; *Chem. Abs.*, **32**, 2654 (1938).

Glasses Permeable to Ultraviolet Radiations

After the discovery of the antirachitic properties of the ultraviolet rays of sunlight (Chapter 38), glass manufacturers sought to develop glasses capable of transmitting all the health-giving solar rays which reach the earth. For use in optical instruments, ultraviolet transmitting glasses had been, however, produced much earlier (about 1907) and Schott and Co. early marketed Uviol glasses, which were, unfortunately, expensive and unstable.[33] According to the historical summary by Davidovitch,[34] Eder and Valenta [35] pointed out that phosphate crown glass has a considerable transparency in the ultraviolet. Zschimmer [36] found that barium oxide had similar properties, but that glasses should be free from alkali metal oxides to increase ultraviolet transparency.[37] Sodium oxide glass is less transparent than that with potassium oxide. Glass with lead oxide is especially poor. Fritsch [38] found a generous proportion of B_2O_3 to confer excellent transparency. A glass of 6 parts of calcium fluoride and 14 of B_2O_3 was said to be transparent down to 1850A. Such glasses have been employed in spectrographic optical systems. Lithium glasses are said to be very transparent to short wave-lengths, but are unstable. While developing certain blue glasses, Luckiesh [39] noticed that cobalt glass appeared to be more transparent than clear glass in the region of 3000A.

Sugie [40] after investigation of the ultraviolet absorption of over fifty samples of soda-lime glasses, found no systematic relation between the absorption and the composition of the glass. Substituting sodium by potassium did not alter the transmission. Phosphorus pentoxide had no effect, but Sb_2O_3, TiO_2, Fe_2O_3, MgO and Al_2O_3 decreased the penetration. His most transparent glass had the composition: Na_2O, 1, CaO, 1.4 and SiO_2, 6 parts; this transmitted through 1.5 mm. wave-lengths as short as 2370A. The least transparent of his series had 1.5 parts of CaO and transmitted down to 2790A. It must be noted, however, that the shortest wave-length which gets through is not as significant a criterion of the quality of a glass as are the fractions of the incident radiation of various wave-lengths which are transmitted. This is true because the drop in the transmission curve is usually not sharp, but extends over several hundred Ångström units in many cases. Sugie found also that up to a certain point, nickel makes glass more transparent to the ultraviolet. When potash rather than soda is present, a nickel glass is black, although it transmits in the ultraviolet. Cobalt can be substituted for nickel in such glasses, but the use of both cobalt and nickel in the same glass diminishes the ultraviolet transmission. In soda-lime (but not potash-lime) glasses, ferric iron lowered the penetrability more than did ferrous iron. Chromium in small quantities had little effect. The effect of manganese is slight up to, but great above, 1 per cent.[41] Locke used a high proportion of alumina and avoided alkalies. In general, permeability increases with the silica content. Barium oxide is superior to lime which, in turn, is better than zinc oxide.

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[33] Rüttenauer, A., *Sprechsaal*, **61**, 449,453 (1928); *Chem. Abs.*, **23**, 2543 (1929).

[34] Davidovitch, P., *J. Opt. Soc. Am.*, **20**, 627 (1930).

[35] Eder, J. M., and Valenta, E., *Denkschriften, Wiener Akad. Wissenschaften Math. Nat. Kl*, **61** (1894).

[36] Zschimmer, E., *Z. Instrumentkunde*, **23**, 360 (1903).

[37] Zschimmer, E., *Physik. Z.*, **8**, 611 (1907).

[38] Fritsch, C., *Physikal. Z.*, **8**, 518 (1907).

[39] Luckiesh, M., *J. Frank. Inst.*, **186**, 111 (1918).

[40] Sugie, S., *Rept. Osaka Ind. Research Lab.*, **5**, No. 11, 1-26 (1924); No. 15, 1-19; **6**, No. 4, 1-26; *Chem. Abs.*, **20**, 3218 (1926).

[41] For further chemical data, see Locke, F. M., *Glass Ind.*, **7**, 136 (1926); *Chem. Abs.*, **21**, 3435 (1927); Weidert, F., *Sprechsaal*, **64**, 992 (1932); Jaeckel, G., *Z. tech. Physik*, **7**, 301 (1926); *Chem. Abs.*, **20**, 3066 (1926); Gilard, P., Swings, P., and Hautot, A., *Rev. belg. ind. verrieres*, **2**, 2, 26, 50, 74, 98 (1931); *Bull. sci. Acad. Roy. Belg.*, **17**, 235, 362 (1931); **15**, 749 (1929); *J. Soc. Glass Tech.*, **15**, 488; *Chem. Abs.*, **26**, 6086 (1932); Fromberg, B. M., and Oshchipkov, F. P., Russian P. 44,317, Sept. 30, 1935; *Chem. Abs.*, **32**, 3112 (1938).

One of the more important lines of development which made possible the commercial production of ultraviolet glasses has been the reduction of those impurities in the raw materials, notably ferric and titanium oxides, which are recognized as increasing the ultraviolet absorption of ordinary silicon-lime-alkali glasses. Hadden[42] produced a glass (4 mm. plates of which are transparent to light waves shorter than 3000A) by reducing the iron impurities to less than 0.055 per cent (as ferric oxide) and the titanium oxide to less than 0.050 per cent. The melting was carried out in a crucible free from these oxides, under non-oxidizing conditions, *e.g.* in the presence of carbon, chromium, uranium, vanadium or nickel. The glass (980A) has a density 2.64 and a refractive index 1.539. The cost of production was above that of window glass, but far below that of quartz.[43] The Corning Co. makes a series of such Corex glasses. According to Gibson of the Bureau of Standards[44] 2 mm. sheets transmit 86 per cent of the radiations at 2900A. This figure is uncorrected for reflection losses of approximately 8 per cent. Corex is available either polished or unpolished, the latter having the same ultraviolet transmission, but not affording clear vision. A change of thickness does not greatly alter the transmission in the biologically important range between 2900 and 3100A.[45] The deleterious effect of ferric oxide was also recognized by Fuwa and Hiraoka,[46] who found the shortest wave-length transmitted by 4.30 mm. of a plate glass containing 0.090 per cent of the oxide to be 3021A. Only 3065A was transmitted by a much thinner plate, 2.78 mm., of a window glass containing 0.103 per cent iron oxide. Starkie and Turner[47] concluded from an extrapolation of their results on the transmission of glasses containing from 0.005 to 1 per cent of iron oxide, that the limiting transmission of a glass free from iron oxide would be 2230A.[48] Klumb and Hasse[49] proposed the use of very thin (10μ) glass windows for scientific work in the ultraviolet region.

By 1926, there had appeared on the market "Vitaglass," probably the first ultraviolet-transmitting glass manufactured in panes on a large scale.[50] The glass was developed by Lamplough, of Trinity College, Cambridge,[51] and was claimed to transmit about 40 per cent of all incident energy in the region 3130 to 2900A. Commercial production began in 1924 in the works of Chance Bros. & Co. and was later extended to the works of Pilkington Bros., Ltd. The absorption by thin glass is shown in Figure 87. Tisdall and Brown[52] found "Vitaglass" to transmit approximately one-fourth of the antirachitic rays of December sunlight.

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[42] Hadden, R., British P. 263,410, July 1, 1926; 298,908, Oct. 5, 1927; 319,337, Sept. 27, 1928, to Corning Glass Works; *Chem Abs.*, **22**, 148 (1928).

[43] Hood, H. P., *Science*, **64**, 281 (1926); *Chem. Abs.*, **20**, 3788 (1926); U. S. P. 1,830,902-4, Nov. 10, 1931. The yellow color may be eliminated by including a compound of zinc. The percentage of silica and B_2O_3 should be 10 to 22 times the total percentage of alkalies and the ratio of SiO_2 to B_2O_3 greater than 5. [German P. 637,438, Oct 28, 1936]

[44] Gibson, K. S., *J. Opt. Soc. Am.*, **13**, 279 (1926).

[45] One way of purifying the raw materials might be to obtain the silica by precipitation from industrial solutions of soluble glass, washing it free from the impurities with sulfuric acid containing hydrogen peroxide. "Osa" participations industrielles, French P. 760,329, Feb. 20, 1934; *Chem. Abs.*, **28**, 3549 (1934). For use of other reagents, see Dusing, W., and Enss, J., German P. 593,687, March 1, 1934; *Chem. Abs.*, **28**, 3549 (1934); Enss, J., and Huniger, M., U. S P. 2,107,935, Feb, 8, 1938, to General Elec. Co.; *Chem. Abs.*, **32**, 2703 (1938).

[46] Fuwa, K., and Hiraoka, T., *J. Japan. Ceram. Assoc.*, **34**, 504 (1926); *Chem. Abs.*, **22**, 487 (1928).

[47] Starkie, D., and Turner, W. E. S., *J. Soc. Glass Tech.*, **12**, 324 (1928); *Chem. Abs.*, **23**, 3550 (1929); see also *J. Soc. Glass Tech.*, **15**, 365 (1931); *Chem. Abs.*, **26**, 3635 (1932).

[48] A number of general review articles covering in more detail the manufacture of special ultraviolet transmitting and absorbing glasses are available: English, S., *Brit. J. Radiol.*, **4**, 724 (1931); Wolf, J., *Ceram. et Verrerie*, 381 (1931); Hoffmann, J., *Sprechsaal*, **65**, 591 (1932); le Braz, J., *Glaces et Verres*, **5**, No. 27, 12 (1932); Grant, J., *Glass*, **9**, 391 (1932); Salmony-Karsten, A., *Chem. Ztg.*, **52**, 269 (1928); *J. Chem. Ind.*, **47**, 36,936 (1928).

[49] Klumb, H., and Hasse, T., *Z. Physik*, **76**, 322 (1932).

[50] *Chem. Age* (London), June 19, 545 (1926).

[51] Lamplough, F. E., *Pottery Gazette*, **54**, 1120 (1929).

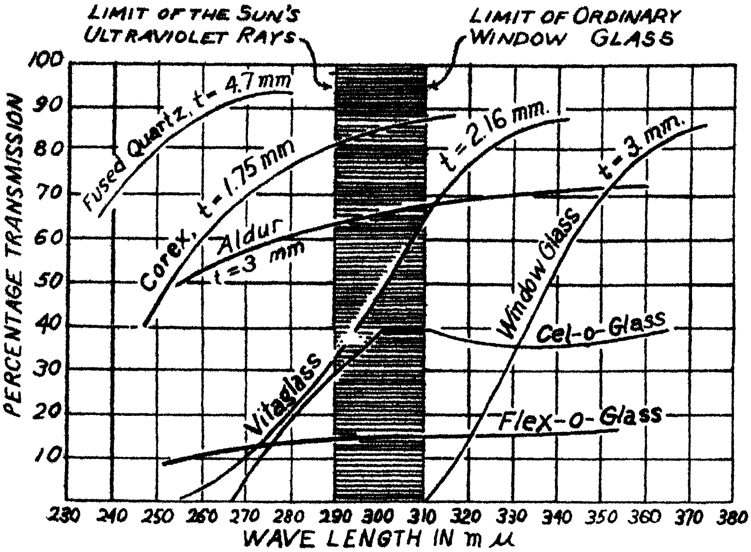

FIGURE 87. Transmission Curves for Vitaglass and Aldur (R. H. Crist, *Industrial and Engineering Chemistry*).

It must be remembered in connection with the use of ultraviolet-transmitting glasses that their effectiveness in the prevention of rickets is limited by the intensity of the incident radiation. If seasonal and atmospheric conditions, or dirt upon the glass, preclude the incidence of more than small quantities of energy in the desired wave-length band upon the glass surface, it is obvious that helpful results cannot be expected from its use. Dust and dirt may reduce the transmission at 3020A by 30 to 40 per cent. There is comparatively little of the valuable ultraviolet in the sunlight of Chicago during the winter months.[53] Clark[54] estimated that a person would receive as much ultraviolet radiation in two minutes in direct sunlight at noon, as in an entire day at 5 meters behind a window of ultraviolet-transmitting glass exposed to the north sky, because the amount of ultraviolet which can enter an ordinary-sized window represents such a small part of that which is available from the entire sky.[55]

Others have attempted to make ultraviolet-transmitting glasses by increasing the silica content of an ordinary glass, *e.g.*, the Quartzlite. Lai and Silverman[56] found the ultraviolet transmission of certain beryllium glasses to be greater than that of ordinary glass, but less than that of magnesium glass. Transmission decreases with increasing beryllia content. Gould, Hampton and Martin[57] suggested the use of a batch giving a finished glass substantially free from dissolved gaseous oxides. The batch may comprise silica, borax and a powdered metal such as zinc, aluminum or tin which combines readily with oxygen and acts as a reducing agent.

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[52] Tisdall, F. F., and Brown, A., *Proc. Soc. Exptl. Biol. Med.*, 24, 449 (1927).

[53] Bundesen, H. N., Lemon, H. B., Falk, I. S., and Coade, E. N., *J. Am. Med. Assn.*, 89, 187 (1928).

[54] Clark, J., *Science*, 68, 165 (1928).

[55] See also Eisenberg, K. B., *Gesundheit Ing.*, 51, 465 (1928); *Chem. Abs.*, 22, 3477 (1928); Long, B., *Science ind.*, 12, 13 (1928).

[56] Lai, C., and Silverman, A., *J. Am. Ceram. Soc.*, 11, 535 (1928); *Brit. Chem. Abs.*, B, 895 (1928); *Chem. Abs.*, 22, 3271 (1928).

English[58] gave a description of the experimental glasses which led to the development of Holviglass. Not only was the effect of iron considered, but it was stated that the admixture of either soda, potash or boric oxide with silica seriously reduces transmission by the latter. The best results were obtained with a soda-boron-silica glass, no relation between silica content and transparency being found. Alkali added as carbonate proved better than when added as the sulfate or nitrate.

Other manufacturers were concerned with the valence state of the iron oxide in the glass. Phelps[59] converted nearly all the iron in the glass to the ferric form by melting the glass under oxidizing conditions or by introducing a nitrate. This is at variance with the conclusions of many others, as Turner[60] who found for glasses containing 0.1 per cent of iron oxide a difference in transmission limits of about 100A between glasses containing the oxide in the ferrous and ferric states, the ferrous transmitting the better. Rose[61] found triavalent iron to cause the absorption of 100 times more ultraviolet than ferrous iron, the limits of transmission being at 3200 and 2200A, respectively.

Various reducing agents have been employed, as charcoal, which tends to make a muddy glass, zinc chloride[62] which makes the glass hazy, stannous oxide[63] or organic compounds such as urea.[64] Aluminum or magnesium powders have been proposed.[65] The addition of manganese oxide has been suggested on the ground that it undergoes oxidation in preference to the iron. Jaeckel[66] describes a glass of high transparency to ultraviolet rays containing at least 10 per cent BaO and not more than 10 per cent of B_2O_3 and not more than 3.5 moles of acid per mole of base. The glass contains no arsenous oxide and practically no ferric oxide. The N.V. Philips' Gloeilampenfabrieken[67] describes a glass substantially free from alkali oxide, consisting of at least 60 per cent of silica together with B_2O_3 and Al_2O_3. The glass softens above 600°. One proposed composition is SiO_2 77.2, Al_2O_3 10.7, CaO 5.4 and B_2O_3 7.0 per cent. Smelt[68] however, uses SiO_2 65, B_2O_3 2, Na_2O 5.5, K_2O 9.5, BaO 15 and ZnO about 3 per cent; iron (in traces) and a fluoride about 1 per cent were incorporated in the mixture.

Beryllium fluoride glasses have been said to transmit to 2200A[69] and Ziegler and Wellmann[70] have suggested alkali-beryllium-borate glasses as substitutes for quartz in optical work. Such a glass, containing 15 to 25 parts of boric acid, 1 to 2 of beryllium carbonate and an alkali carbonate equivalent to 3 to 6 parts of lithium carbonate, is reported to be applicable for lenses, prisms and mercury-vapor lamps. Draisbach and Draisbach[71] fuse beryllium ortho- or meta-phosphate, and add the corresponding salts of calcium, magnesium or sodium.

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[57] Gould, C. E., Hampton, W. M., and Martin, H. S., British P. 312,728, March 19, 1928; *Chem. Abs.*, **24**, 937 (1930).

[58] English, S., *Glass*, **5**, 338 (1928); **8**, 52 (1931); *Chem. Abs.*, **23**, 252 (1929).

[59] Phelps, D. V., British P. 320,904, July 25, 1928, to Pilkington Bros.; *Chem. Abs.*, **24**, 2566 (1930).

[60] Turner, W. E. S., *J. Soc. Chem Ind.*, **48**, 65T (1929); *Chem. Abs.*, **23**, 3063 (1929); *Brit. Chem. Abs.*, **B**, 355 (1929); see also Andresen-Kraft, C., *Glastech. Ber.*, **9**, 577 (1931).

[61] Rose, G., *Sprechsaal*, **62**, 314, 333, 352, 375 (1929); *Chem. Abs.*, **23**, 4544 (1929).

[62] German P. 493,857, Dec. 30, 1925, to Deutsche Spiegelglas A.-G.; *Chem. Abs.*, **27**, 578 (1933).

[63] German P. 528,394, July 9, 1929, to Deutsche Spiegelglas A.-G.

[64] German P. 524,374, May 10, 1927, to Deutsche Spiegelglas A.-G.

[65] Vargin, V. V., *Keram i Steklo*, 7, No. 1, 4 (1931); Wollner, F., Wollner, R., and Nikolai, F., British P. 339,903, March 12, 1929; Austrian P. 120,674, Oct. 15, 1929; French P. 691,805, March 12, 1930.

[66] Jaeckel, G., German P. 583,001, Aug. 26, 1933, to Sendlinger optische Glaswerke; *Chem. Abs.*, **28**, 277 (1934).

[67] British P. 440,778, Jan. 6, 1936, to N. V. Philips' Gloeilampenfabrieken; see also, Elenbaas, W., Jonas, G. B., and van Wyk, A., Canadian P. 373,786, May 17, 1938; *Chem. Abs.*, **32**, 5316 (1938).

[68] Smelt, J. A. M., U. S. P. 2,056,627, Oct. 6, 1936; *Chem. Abs.*, **30**, 8550 (1936).

[69] Heyne, G., *Angew. Chem.*, **46**, 473 (1933); Salmony-Karsten, A., *Sklarske Rozhledy*, **11**, 35 (1934); *Chem. Abs.*, **29**, 6713 (1935).

Another trend is the development of lithium-beryllium-borate "Getan" glass, which is not hygroscopic and does not decompose in the air, but is transparent to ultraviolet and x-rays.[72] One mm. of the glass transmits 80 per cent of the energy of the wave-length 2537A.

The Philips Lamp Co.[73] suggest for bulbs for transmitting ultraviolet a clear, transparent glass containing a fluoride and practically free from lead, antimony or titanium. Locke and Locke[74] melt a fluorine-containing batch (SiO_2 35.5-40, H_3BO_3 16.5-32.5, Al_2O_3 21-27 and CaO 11-17 per cent with calcium fluoride) in a carboniferous container. Fuwa and Suzuki[75] use 1 to 5 per cent sodium fluoride and 1 to 5 per cent ammonium oxalate or tartrate.

A glass of high resistance to water and permeable to the ultraviolet may be composed for the greater part of barium metaphosphate, along with metaphosphates of calcium and magnesium.[76] Grimm and Huppert[77] replace the silica normally used in making glass wholly or in part by $AlPO_4$ in the proportion of one molecule for every two of silica replaced. Ammonium salts, particularly phosphates, may be added to the frits of phosphate glass.[78]

Other Ultraviolet-Transmitting Materials. In the preparation of window-glass substitutes, materials quite unlike glass have at times been employed. Thus a urea-formaldehyde condensation product was introduced for this purpose by the Luco Products Corporation under the name of Aldur. Crist[79] gave a curve for its transmission and compared it with "Vitaglass." (Figure 87.) He found also that when exposed at 65°C. at 8 inches from a 220-volt mercury lamp, no change in transmission of the 3020A region was apparent after 41 hours, a fairly severe test. The transmission of the 2540A line was decreased from 48 to 40 per cent in 18 hours. Data for "Plexiglas" (Acryloid) have been given by Jakobson.[80]

A filter suitable for glazing windows which transmits to 2900A is a polymerized vinyl acetate, reënforced with a reticulated material as a wire mesh or woven

[70] Ziegler, W., and Wellmann, M., *Z. tech. Physik*, 14, 288 (1933); *Chem. Abs.*, **27**, 4366 (1933); Wellmann, M., German P 585,816 (1933); *Chem. Abs.*, **28**, 1492 (1934).

[71] Draisbach, H., and Draisbach, F., British P. 436,426, Oct. 10, 1935; French P. 785,966, Aug. 23, 1935.

[72] Hertsriken, S. D., *Tech. Phys. U.S.S.R.*, 3, 336 (1936); *Chem. Abs.*, **31**, 4782 (1937).

[73] British P. 373,378, May 29, 1930, to N. V. Philips' Gloeilampenfabrieken; *Chem. Abs.*, **27**, 3306 (1933).

[74] Locke, F. M., and Locke, F. J., U. S. P. 1,886,280, Nov. 1, 1932, to Corning Glass Co.; *Chem. Abs.*, **27**, 1470 (1933).

[75] Fuwa, K., and Suzuki, S Japanese P. 101,817, July 1, 1933; *Chem. Abs*, **28**, 5617 (1934); Fuwa, K., U. S. P. 1,971,309, Aug. 21, 1934, to General Electric Co.; *Chem. Abs.*, **28**, 6542 (1934).

[76] French P. 751,524, Sept. 5, 1933, to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, **28**, 1159 (1934); Kaufmann, W., and Bungartz, E., U. S. P. 2,031,958; German P. 634,698-9 and 636,035; *Chem. Abs.*, **31**, 828 (1937). Aluminum may also be added to increase the water resistance.

[77] Grimm, H. G., and Huppert, P., German P. 580,295, July 8, 1933; *Chem. Abs.*, **27**, 388, 4895 (1933).

[78] French P. 775,451, Dec. 28, 1934, to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, **29**, 2680 (1935); British P. 424,366, Feb. 20, 1935. For other patents on ultraviolet glasses, see German P. 527,053, Dec. 16, 1928, to Deutsche Gasglühlicht Auer-Ges.; Gericke, I., German P. 527,404, Jan. 17, 1930; Weld, H. W., U. S. P. 1,845,376, Feb. 16, 1932; *Chem. Abs.*, **26**, 2294 (1932).

[79] Crist, R. H., *Ind. Eng. Chem.*, **20**, 1367 (1928); see also Katowaki, H., and Kasai, E., *Repts. Imp. Ind. Research Inst., Osaka*, **13**, No. 3 (1932); *Chem. Abs.*, **27**, 1719 (1933).

[80] Jakobson, T., *Tek. Tid.*, **67**, Uppl. A-C, Kemi, 15 (1937); *Chem. Abs.*, **31**, 4210 (1937).

fabric.[81] It has been proposed to make a fabric of threads formed of a core of material opaque to light, such as cotton, carrying a coating such as regenerated cellulose, capable of transmitting ultraviolet.[82] The Vitalite Co. produces a fine wire cloth coated with a cellulose acetate composition, yielding a flexible wire product, possessing the advantages of weather resistance and transmitting the ultraviolet range. Ramstetter [83] suggested the use of transparent condensation products of carbamide and its derivatives with substances capable of yielding formaldehyde as a substitute for quartz glass; the condensation products absorb ultraviolet rays but slightly. Walsh [84] coats a wire cloth with an ultraviolet-transparent film of cellulose acetate 100, triphenyl phosphate 10-20 and dibutyl tartrate 10 to 20 parts.

In some instances [85] "Vitaglass" or quartz glass may be made into a laminated glass by the aid of acetylcellulose applied in the form of thin sheets. Zimmerli [86] prepared an ultraviolet-transmitting material by evaporation of a cellulose ester and a plasticizer, such as diethyl phthalate. Polymerized vinyl compounds, including vinyl acetate, chloroacetate and styrene, may be used in single or laminated sheets in making reënforced glass substitutes permeable to ultraviolet light.[87]

Data on the Transmission of Various Ultraviolet-permeable Materials. Starkie and Turner [88] determined the transmissions of 2 mm. thicknesses of eight commercial glasses over the range 7000 to 2000A. Corex A was found to transmit 89 per cent in the therapeutic region (2950-3150A). The remaining glasses showed: "Sanalux," 73 per cent, "Sun Ray" 62, "Holvi" 61, "Viat" 54, "Helio" 53, "Uviol" 45, "Quartz-Lite," 4 per cent. Ordinary window glass transmits only 1 per cent of these rays. Corex had the lowest iron content, 0.012 per cent, that of the remaining samples ranging from 0.021 to 0.054 per cent. After a 12 weeks' exposure to sunlight, Corex became stained with a white film. But on being cleaned, it showed undiminished transmission. When artificially aged under the carbon arc, the greatest change occurred in the first two hours, the fall in transmission coinciding with a decrease in the proportion of ferrous oxide to total iron oxide in the glass. Turner [89] finds this change can be reversed by heating the glass to 600-700°C.[90] Hoffman [91] believes the solarization to incolve the formation of ferrites.

According to Bundesen, Lemon, Falk and Coade,[92] incandescent 300-watt lamps with ordinary glass bulbs emitted radiations comparable to Chicago sunlight in the winter months and Vitaglass bulbs emitted radiations as far as the region 2800 to 2900A.

The results of the physical transmission of Corex received confirmation in prophylactic animal tests against rickets, using Uviarc irradiation through the samples.[93] Growth curves, calcium and phosphorus determinations in the blood serum, x-rays of the tibiae and femurs, bone ash and pathological studies agreed in showing that irradiation through Corex was as effective as direct irradiation. "Vitaglass" was less effective and animals irradiated through ordinary window glass gave results very similar to those found in non-irradiated animals. Wyman [94] also conducted therapeutic tests on rachitic children with similar results.

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[81] Greider, C. E., U. S. P. 1,786,205, Dec 23, 1930, to National Carbon Co. Note also British P. 366,077, June 29, 1929.

[82] Millen, J., U. S. P. 1,910,850, May 25, 1933; *Chem. Abs.* **27**, 4101 (1933).

[83] Ramstetter, H., German P. 416,753, Jan. 31, 1923, to Badische Anilin und Soda Fabrik.

[84] Walsh, J. F., U. S. P. 1,931,518, Oct. 24, 1933, to Celluloid Corp.; *Chem. Abs.*, **28**, 637 (1934).

[85] Colefax, M. A., British P. 323,671, *Kunstoffe*, June, 139 (1930). Dreyfus, C., U. S. P. 1,924,398, Aug. 29, 1933; *Chem. Abs.*, **27**, 5503 (1933); U. S. P. 2,002,082, May 21, 1935; *Chem. Abs.*, **29**, 4539 (1935); Canadian P 330,842, *Chem. Abs.*, **27**, 3375 (1933); British P. 306,397, Feb. 18, 1928, to British Celanese, Ltd.; *Chem. Abs*, **23**, 5021 (1929).

[86] Zimmerli, A., U. S. P. 1,842,640, Jan. 26, 1932, to Acetol Products; *Chem. Abs.*, **26**, 1781 (1932).

[87] British P. 366,077, July 29, 1929, to Celluloid Corp.; *Chem. Abs.*, **27**, 3047 (1933).

[88] Starkie, D., and Turner, W. E. S., *J. Soc. Glass Tech.*, **12**, 306 (1928); *J. Soc. Chem. Ind. Supplement*, March 29, 245 (1929). Other data have been given by Winther, C., *Z. wiss. Phot.*, **25**, 230 (1928), and by Harris, D. T., *J. Sci. Instruments*, **6**, 2 (1929).

[89] Turner, W. E. S., *J. Soc. Chem. Ind.*, **48**, 65 (1929).

[90] Compare Hood, H. P, U. S. P. 1,889,067, Nov. 29, 1932; *Chem. Abs*, **27**, 1470 (1933). British P. 298,908, Nov. 14, 1928, to Corning Glass Co., *Chem Abs.*, **23**, 3066 (1929). Hood heats to 550° for 15 minutes or to 400°C. for one hour.

[91] Hoffmann, J., *Glastech. Ber*, **12**, 53 (1934); *Chem. Abs.*, **28**, 4554 (1934).

[92] Bundesen, H. N., Lemon, H. B., Falk, I. S., and Coade, E. N., *J. Am. Med. Assoc.*, **89**, 187 (1928).

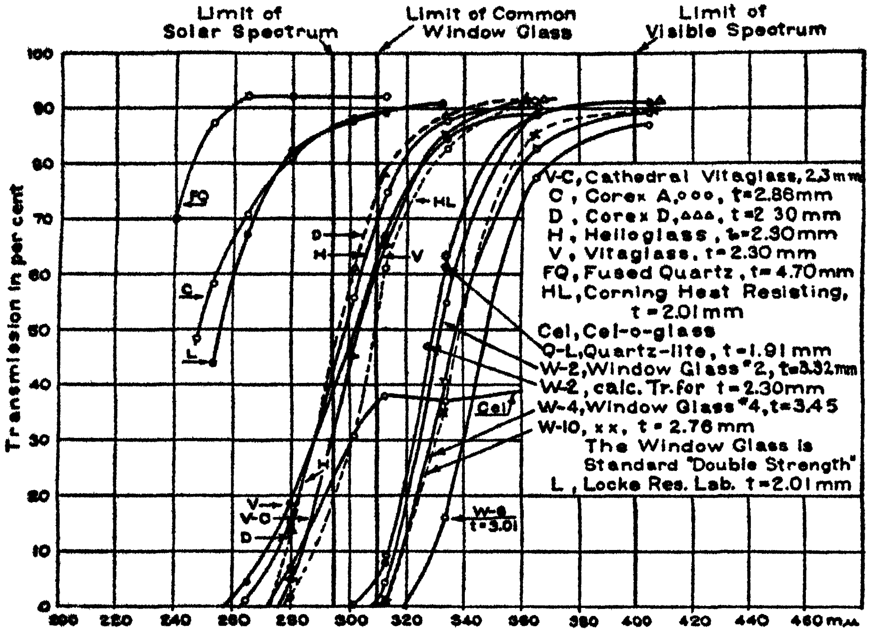

FIGURE 88. Transmission Curves of Ultraviolet-permeable Glasses. (Coblentz and Stair, *Journal Research, Bureau of Standards*).

Durability of Ultraviolet-transmitting Materials. The question of solarization, or the effect of prolonged exposure to the sun or other sources of ultraviolet is of importance since ultraviolet transmitting materials are intended for use over long periods. The discoloration of glass in the globes surrounding street arc lights is familiar to everyone. Eckert [95] noted that glasses containing a small percentage of cerium rapidly assume a brown color in day or artificial light due to the action of ultraviolet rays, the glass becoming fluorescent and phosphorescent. The brown color fades irreversibly on heating.

In 1927 the Bureau of Standards had found that nearly all of the glasses then in use undergo a photochemical action, the glass decreasing greatly in transparency in the region 2900 to 3100A when exposed to ultraviolet radiations.[96] The materials fell into three classes (Figure 88): (1) Fused quartz, Corex and Locke glass, which have an initial transmission of the 3020A line of over 85 per cent and show little or no decrease in solarization; (2) "Vitaglass" and Helioglass, with initial transmission of 45-55 per cent, decreasing to about half on exposure; (3) Quartzlite and common window glass, with initial transmissions of 0 to 1.5 per cent and no change on exposure. Cel-O-glass becomes opaque to this line after 25 hours' exposure to the quartz mercury arc, but a sample that had been exposed to the sun for 400 hours during the months of April to October decreased but little in transparency. On the other hand, samples that had transmitted 30 per cent when new, transmitted only 5 to 10 per cent after having been exposed on the side of a building day and night from April to December, showing that the change in transparency may depend upon weather conditions. This product has been employed in poultry houses for preventing leg weakness in chicks.[97] Russell and Howard[98] found that the value of Cel-O-glass for this purpose was not diminished after exposure for 13.5 months.

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[93] Wyman, E. T., Holmes, A. D, Smith, L. W., Stockbarger, D. C. ,and Piggott, M. G., *Am. J. Diseases of Children*, 37, 473 (1929), *Chem. Abs.*, 23, 3064 (1929).

[94] Wyman, E. T., *Boston Med. & Surg. J.*, 197, 376 (1927).

[95] Eckert, F., *Z. tech. Physik*, 7, 300 (1926); Eckert, F., and Schmidt, K., *Glastech. Ber.*, 10, 80 (1932); *Chem. Abs.*, 27, 1468 (1933).

[96] Bureau of Standards, *J. Frank. Inst.*, 666 (1927); *Letter Circular No. 235, 3rd Revision; J. Research Bur. Standards*, 3, 629 (1929); Coblentz, W. W., and Stair, R., *Trans. Illum. Eng. Soc.*, 23, 1121 (1928); *Chem. Abs.*, 23, 944 (1929).

In more recent work, Coblentz[99] reported improvement in the quality of certain of these glasses. He summarized data (based on samples secured prior to May 1, 1930) based on exposure of the glasses for ten hours at 15 cm. from a 110-volt, horizontal Uviarc and of duplicate samples exposed to the sun for five to twelve months, using an average thickness of 2.3 mm. (Table 15.)

Table 15.—Transmission of Ultraviolet Rays by Glass.

		Average Per Cent Transmission		
Trade Name	Number of Samples	New	After Uviarc	After Sun
Quartz glass	1	92	92	92
Corex D	3	61	59	60
Newglas	3	63	50	57
Uviol-Jena	3	67	48	53
Helioglass	8	64	45	53
Sunlit	3	71*	42*	51
Vitaglass	20	58	33	42
Common window	3	0	0	0

* Improved material later examined averaged 72 per cent when new and 47 per cent after exposure to the mercury lamp.

Rüttenauer[100] found the foreign products Osram UV, Ultraviol, Brephos, Bios, Vita and Schott's UV to show only small ageing. He has also considered the effect of heat on the rate of ageing, a matter of importance when such glasses are used in lamp bulbs. Nitchie and Schmutz[101] found in some cases an increase in short-wave transmission at 450°C.

Coblentz and Stair[102] studied the effects of various filtered ultraviolet wavelengths in producing changes in the ultraviolet transmission of soda-lime-silica glass. The work was done in the hope of accelerating stabilization of the transmission. This effort proved impracticable because of antagonistic effects about 3650A which reversed the action of shorter wave-lengths. No wave-length shorter than 3650A was found to have the exclusive property of increasing or decreasing the ultraviolet transmission of these glasses. A phosphate-lime glass has its transmission lowered by wave-lengths shorter than 2900A, and this could not be retarded by exposure to the region 2970-3650A, in contrast to the soda-lime-silica glasses. Stockbarger [103] is of the opinion that solarization, at least so far as it relates to the application of ultraviolet glasses in photochemical apparatus, is not serious. Solarization takes place within a short length of time, after which the characteristic properties of the glass are retained for a considerable time. It has been said that when kept in the dark, glass, previously solarized by the mercury arc, does not regain any of its lost ultraviolet transparency, but that it does regain transparency when exposed to sunlight directly or through window glass or when exposed to the mercury arc through a thick layer of window glass. It is also pointed out [104] that the use of the mercury-vapor lamp to predict the loss of transparency of glass when exposed to sunlight may give misleading results.

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[97] Cochran, R. L., and Bittenbender, H. A., *Bull.* 246, *Iowa State College, Agr. Expt. Sta.*, 1928.

[98] Russell, W. C., and Howard, C. H., *Poultry Sci.*, 8, 290 (1929).

[99] Coblentz, W. W., *Trans. Illum. Eng. Soc.*, 26, 610 (1931).

[100] Rüttenauer, A., *Sprechsaal*, 61, 449 (1928).

[101] Nitchie, C. C., and Schmutz, F. C., *Science*, 71, 590 (1930).

[102] Coblentz, W. W., and Stair, R., *J. Research Bur. Standards*, 13, 773 (1934); *Proc. Nat. Acad. Sci.*, 20, 630 (1934); *Chem. Abs.*, 29, 1597 (1935).

The tendency of an ultraviolet-permeable glass to lose transparency may be counteracted by the incorporation of a small proportion (0.05-0.5 per cent) of manganese oxide.[105] The I. G. Farbenindustrie [106] describes an ultraviolet-permeable phosphate glass (stable to irradiation) which was said to have the following composition: potassium carbonate 13.77, potassium nitrate 6.71, calcium carbonate 8.93, barium carbonate 3.22, magnesium carbonate 18.53, B_2O_3 31.04, alumina 28.80 and secondary ammonium phosphate 48.70 parts. Huppert and Wolff [107] state that the important phosphatic glasses may be rendered more stable to radiations by including an ammonium salt (phosphate, carbonate or nitrate). The formation of blisters may be avoided by the addition of an oxidizing agent.

Lasse [108] finds irradiation of ordinary and Uviol plate glass with wave-lengths 3000 to 4000A from a Hanau silica burner diminishes the transparency for these rays to 34 and 19 per cent respectively. The coloration of manganese-containing glass by ultraviolet rays is said by Cross [109] to be due to light of a wave-length only slightly greater than 2900A, the absorption limit of the glass. The tinting takes place only near the surface, and is hastened by heating. Decolorization is accelerated by heat or visible light.

The fluorescent effects produced by ultraviolet on various glasses are sufficiently different to afford indications of the nature of their coloring materials.[110] Shrum, Patten and Smith [111] found heat treatment at 300°C. to remove the ability of ultraviolet light or even x-ray solarized glasses to luminesce before the quartz mercury arc. The transmission in the ultraviolet was restored as the thermoluminescence disappeared.[112]

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[103] Stockbarger, D. C., *Science*, **70**, 73 (1929).

[104] Wood, A. R., and Leathwood, M. N., *Nature*, **124**, 441 (1929).

[105] British P. 291,468, June 4, 1927, to Soc. Anon. des Manufactures des Glaces et Produits Chimiques de Saint-Gobain, Chauny, et Cirey; *Chem. Abs.*, **23**, 1235 (1929); *Brit. Chem. Abs.*, **B**, 145 (1930); French P. 647,188, June 4, 1927; Long, B., U. S. P. 1,779,176.

[106] British P. 424,366, Dec. 2, 1933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.*, **B**, 406 (1935).

[107] Huppert, P., and Wolff, H., German P. 630,347, Oct. 19, 1935; U. S. P. 2,077,481; see also Hoffmann, J., *Sprechsaal*, **70**, 517, 529 (1937); *Chem Abs.*, **32**, 5592, 8717 (1938).

[108] Lasse, R., *Helv. Phys. Acta*, **5**, 92 (1932); *Chem. Abs.*, **26**, 6086 (1932).

[109] Cross, C. L., *Phys. Rev.*, **27**, 108 (1926).

[110] Lester, W. R., *Glass Ind.*, **12**, 83 (1931).

[111] Shrum, G. M., Patten, C. G., and Smith, H. D., *Trans. Roy. Soc. Canada*, **22**, (3), 433 (1928); *Chem. Abs.*, **23**, 2003 (1929).

[112] For further discussion of the theory of solarization processes, see Klemm, A., and Berger, E., *Glastech. Ber.*, **13**, 349 (1935); Hoffmann, J., *Ibid.*, **12**, 53 (1934); *Chem. Abs.*, **28**, 4554 (1934); *Glastech. Ber.*, **13**, 47 (1935); *Brit. Chem. Abs.*, **B**, 1093 (1936); *Glastech. Ber.*, **14**, 281 (1936); *Glass*, **13**, 419, 433 (1936).

FILTERS

In the visible region, a great number of screens or filters have been prepared for the isolation of definite wave-length regions; certain of these find wide employment in photography, especially in color photography. Others are of importance in stage lighting. The properties of these and other filters are due to the ability of the substances employed to absorb radiations of definite frequencies selectively. Substances which are highly absorbing even when present in extremely dilute solutions are the most satisfactory materials for filters since, when taken in higher concentrations, they exhibit a sharp cut-off of radiations transmitted. This means that the wave-length range between nearly complete transmission and nearly complete absorption is very narrow, comprising only a few Angström units. Since but few substances meet this requirement, filters are best used with discontinuous line sources of radiations as the mercury arc.

The theory of the application of glass filters to the measurement of the intensity of groups of lines emitted by a source has been discussed in detail by Stockbarger and Burns.[113] Errors may arise because of failure to take into account the fact that the transmission curves of filters are not rectangular but sloping; if the cut-off be taken as the wave-length at which the transmission becomes zero, the results will be greatly in error. These authors recommend that the effective "cut-off" be considered to be the point at which the energy transmitted by the filter below the "cut-off" equals that which is selectively absorbed above it. In order to locate this point there needs to be known, besides the transmission characteristics of the filter, the energy distribution of the source in the region in which the filter transmits poorly.

Particular attention has been devoted to the theory relating the slope of the absorption curve of a filter material to the effectiveness with which it will separate a given line from close neighboring lines, by Dahm,[114] who was especially interested in developing filters suitable for use in studies of the photoelectric effect. He gives absorption data for over twenty organic compounds, plotted in an unusual manner adapted to his theoretical treatment.

Stability is another quality desired in a filter material. The absorbed radiations must produce or initiate only very slow photochemical changes. Otherwise, the nature of the filtering material will change during its use, and the products formed may absorb quite differently, resulting in a change in the filtering properties with use. In the colored filters employed in the visible region, these changes are usually slow enough so that the filters are stable for considerable periods. Liquid filters composed of solutions of colored salts or dyes in cells with parallel glass sides, or solid filters of glass or stained films of collodion or more usually gelatin, are commonly employed. Simple inorganic salts when available are usually more stable and more readily prepared in definite concentrations than are the organic dyes, which may be of less definite purity and which are frequently subject to fading.

In the ultraviolet region, the energies associated with the various wave-lengths absorbed by the filters are far greater than in the visible region. In this region, therefore, it is necessary to check the filtering characteristics of filters at frequent intervals or else to use solutions which flow slowly through the filter cells.

Filters capable of transmitting only narrow spectral bands or individual lines are rare. It is usually necessary to use filters to supply radiations from which certain more or less broad spectral regions have been excluded. In the visible region, there is a filter arrangement which transmits only the green line of the mercury arc. This filter is didymium glass, which has a sharp absorption band between 5500 and 5800A. Used with a strong yellow filter, the filter yields the green line in high intensity and supplies a strong source of nearly monochromatic light. Glasses to emphasize color contrasts may contain neodymium oxide.[115] A discussion of filters in the infrared and visible regions lies beyond the scope of this book.[116] Many photographic filters have the drawback of fluorescing and so causing a loss of contrast.[117]

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[113] Stockbarger, D. C., and Burns, L., *Phys. Rev.*, **34**, 1265 (1929).

[114] Dahm, T. M., *J. Opt. Soc. Am.*, **15**, 266 (1927).

Filters for Black Light. Among the earliest ultraviolet filters were those designed to exclude the visible rays and transmit only the invisible ultraviolet. Such filters have recently acquired new importance with the development of methods of fluorescence analysis under ultraviolet irradiation. By their use, fluorescent effects in great variety are easily secured. In a darkened room irradiated only by ultraviolet rays, the teeth, eyes and even the fingernails glow with a weird yellowish fluorescence. Artificial teeth do not become fluorescent but appear black. The beautiful fluorescent effects characteristic of various minerals have been so frequently exhibited in museums as to be familiar to almost everyone. Uranium nitrate shines when exposed to ultraviolet rays, and vapors of mercury may be seen rising from a body of mercury even at room temperature when photographed by ultraviolet rays.

A filter for this purpose consisting of quartz coated with silver was employed by R. W. Wood in 1911 in a demonstration at the Royal Institution of the fluorescent effects produced by ultraviolet radiations. Among the striking effects there demonstrated was the fact that white zinc oxide comes out black. Photographs of flowers taken through a quartz lens were also exhibited. A number of flowers which, when photographed by visible light, came out in widely different shades, when white or colored, left a black or dark gray image when photographed by ultraviolet light. Another group of flowers to which Michaud and Tristan [118] gave the name of ultraviolet flowers, were reproduced by ultraviolet much as by ordinary light. These flowers were yellow under ordinary light. These authors prepared a lens which excludes light other than ultraviolet by precipitating on a quartz lens a layer of silver from an alkaline silver solution by means of a 10 per cent solution of milk sugar.

Silver, either in the form of plates or in the colloidal state, is not entirely satisfactory since its absorbing capacity ends at about 4000A [119] and with high concentrations of silver, absorption in the short ultraviolet region is noted. Brock [120] prepared a silver filter by exposing a lantern slide, developing it to a brown color and then stripping off the emulsion and supporting the latter between two plates of Uviol or "Vitaglass." The resulting filtering action is believed superior to that of either sputtered or chemically deposited films, maximum transmission occurring at about 3000A.

Wood [121] suggested the use of nitroso-dimethylaniline in making filters transparent only to ultraviolet rays. This compound, however, transmits only the longer ultraviolet. Absorption spectra for the aniline derivative and for methyl violet have been determined by Pospelov and Yampolskii.[122]

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[115] Weidert, F., British P. 338,334, Dec. 15, 1928; *Chem. Abs.*, **25**, 2259 (1931).

[116] See Mees, C. E. K., in Glazebrook's Dictionary of Applied Physics, IV; Potapenko, G., *J. Russian Phys. Chem. Soc.*, **48**, 790 (1916); *Brit. J. Phot.*, **68**, 507 (1921).

[117] Bäckström, H., and Johansson, R., *Z. wiss. Phot*, **36**, 194 (1937); *Chem. Abs.*, **31**, 6123 (1937); **32**, 2837 (1938).

[118] Michaud, G., and Tristan, F, *Scientific American*, **111**, 301 (1914).

[119] See also Goos, F., *Z. Physik*, **100**, 95 (1936); for gold films, see Goos, F., *Z. Physik*, **100**, 606 (1937).

[120] Brock, G. C., *Sci. Proc. Roy. Dublin Soc*, **20**, 563 (1933); *Brit. J. Phot.*, **80**, 495 (1933); *Chem. Abs.*, **27**, 5262 (1933).

[121] Wood, R. W., *Phil. Mag.*, **5**, 257 (1903); see also Lehmann, H. *Physik. Z.*, **11**, 1039 (1910).

Winther and Mynster [123] suggested a filter which transmits a range of 4050 to 3200A with a maximum at 3750A. It consists of a one centimeter cell containing a 2.5 per cent solution of copper sulfate with six times the quantity of ammonia necessary to redissolve the precipitate which first forms. This is combined with a one centimeter cell of a 0.045 per cent solution of fuchsine in water. In another filter, the dye is replaced by a 0.1215 per cent solution of potassium chromate, the maximum transmission in this case being at 3130A. With an increasing excess of ammonia, copper sulfate solution becomes more transparent, especially in the ultraviolet; the maximum transparency is attained when the ammonia present is four times the quantity necessary to redissolve the precipitated copper hydroxide, and then extends from 4500 to 3000A.

Lamps in Corex are made impermeable to visible rays, while retaining their ultraviolet transmission, by dipping in an alcoholic suspension of P_2O_5 68, CaO 27, B_2O_3 5 per cent, with cobalt oxide to color, or of SiO_2 68.5, B_2O_3 23, Na_2O 6.5 and Al_2O_3 2 per cent. The lamps are then heated in a furnace.[124] An envelope to serve this same purpose has been suggested by Gillard and West.[125] It comprises glass with nickel oxide and a little copper oxide. The maximum transparency is at 3650A, falling rapidly on either side of this wave-length. Another means of securing ultraviolet radiation with but one per cent of the visible is by operation of a small mercury arc at 5 amperes and 15 volts.[126]

Filters Excluding Various Ultraviolet Regions. Some of the glasses whose transmission characteristics have been discussed in the preceding section, have been employed as filters for various wave-lengths in the ultraviolet region. Their usefulness for this purpose is somewhat limited by the lack of sharpness of their transmission curves.[127]

Corning glass filters [128] are most satisfactory where their thickness and consequent bulk are not objectionable, and where appreciable heat must be dealt with. As is apparent from Figure 89, they generally have rather broad but high transmission characteristics and hence are used in combination to secure the desired effects. A nickel oxide glass (Corning) transmits 3660A. Further data on the filtering properties of various glasses by Taylor and Holladay are recorded in Figure 90.[129]

In order to prepare a ray filter which will allow only waves of a definite length to pass, Peskov [130] states that it is necessary to calculate the coefficient of absorption of the substance and then determine the density and thickness of the solution so that the desired quantity of energy of a definite wave-length will pass the filter.

Gases have been widely used as filters in the ultraviolet. The coefficients of absorption of a number of gases for light after passage through quartz windows has been measured by Varley.[131] It is the filtering characteristic of oxygen (aside

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[122] Pospelov, A., and Yampolskii, B., *J. Phys. Chem. (U.S.S.R.)*, **3**, 514 (1932); *Chem. Abs.*, **27**, 1826 (1933).

[123] Winther, C., and Mynster, E. H., *Z. wiss Phot.*, **24**, 90 (1926); *Chem. Abs.*, **20**, 3249 (1926).

[124] French P. 762,053, April 3, 1934, to Compagnie des lampes. See also Eidinow, A., and Hewittic Electric Co., Ltd., British P. 307,961, Dec. 13, 1927; *Chem. Abs*, **24**, 29 (1930).

[125] Gillard, F. W., and West, D. L., British P. 294,949, Apr. 1, 1929; *Chem. Abs.*, **23**, 1827 (1929). Note also Sugie, J., *J. Japan. Ceram. Assoc.*, **34**, 24 (1926); *Chem. Abs.*, **22**, 487 (1928).

[126] Zahour, R. L., *Elec. J.*, **30**, 453 (1933).

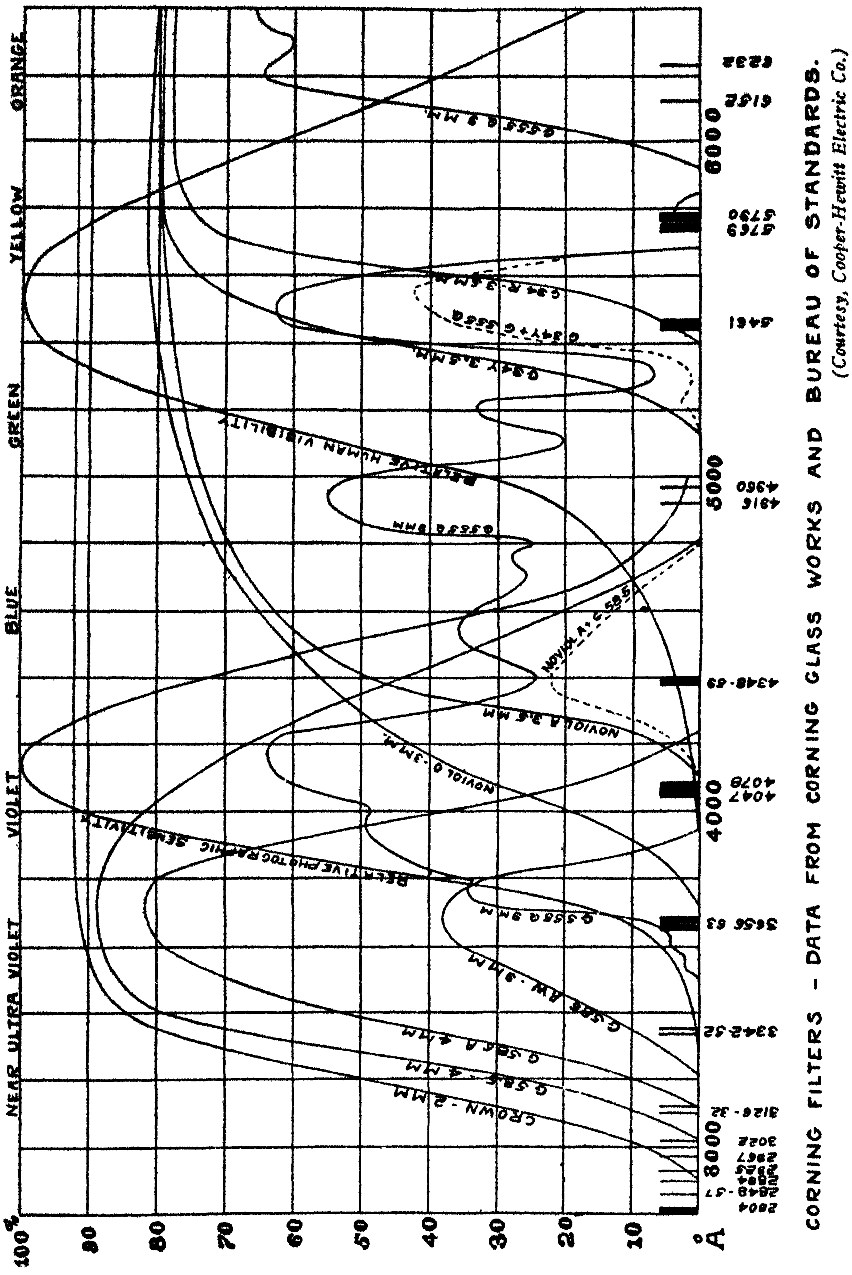
[127] Mannich, C., *Chem. Ztg.*, **33**, 1167 (1909).

[128] Gibson, K. S., and McNicholas, H. J., *Bureau of Standards Tech. Papers*, 119 (1919); 148 (1920); *Sci. Paper* 325 (1918).

[129] Taylor, A. H., and Holladay, L. L., *Trans. Illumin. Eng. Soc.*, **26**, 711 (1931).

[130] Peskov, N. P., *J. Phys. Chem.*, **21**, 381 (1917); *Z. wiss. Phot.*, **18**, 235 (1919).

[131] Varley, W. M., *Proc. Camb. Phil. Soc.*, **12**, 510 (1904).



(*Courtesy, Cooper-Hewitt Electric Co.*)

FIGURE 89. Transmission Curves for Corning Glass Filters.

from the limitations of the output of the source employed) which sets the short wave limit in most photochemical work, since it begins to absorb strongly at 1860A, while nitrogen is transparent even at 1250A. According to Peskov, chlorine is frequently useful, since its maximum absorption is in the region 3800-3000A. Bromine vapor cuts out the visible part of the spectrum to 3800A and its absorption capacity ends slightly beyond the point where chlorine absorption begins.[182] In water solutions, the absorption characteristics of these two elements change because of the formation of complex molecules of halogen and water.

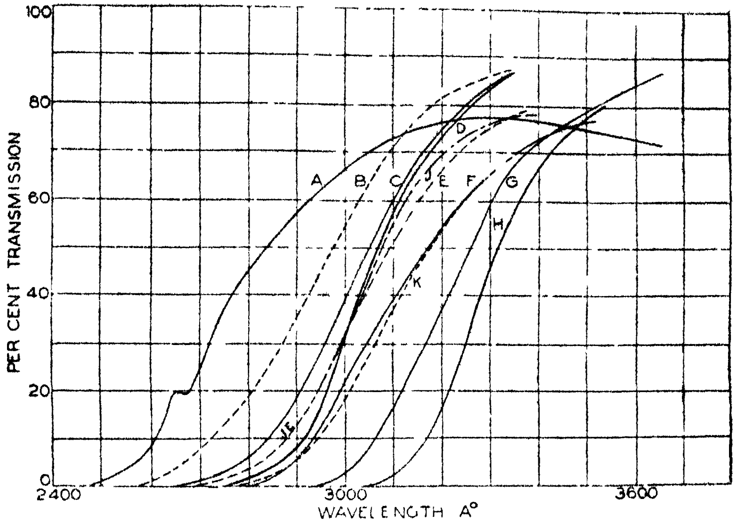


FIGURE 90. Spectral Transmission Curves of Glass Filters (Taylor and Holladay, *Transactions Illumination Engineering Society*). A, red-purple Corex A, 4.21 mm. thick; B, microscope glass, 0.18 mm.; C, microscope slide, 0.96 mm.; D, "Pyrex," 1.05 mm.; E, 2 layers of microscope glass, 0.36 mm. total; F, 3 layers of microscope glass, 0.55 mm. total; G, "Pyrex," 2.99 mm; H, Quartzlite, 2.02 mm.; J, Helioglass, 2 mm.; K, "Vitaglass," 2.77 mm.

Use has been made of chlorine and bromine filters in the work of Svedberg and Nichols[133] on the determination of the molecular weight of egg albumin by ultracentrifugal methods. In this work, it was necessary to determine the concentration of the protein solution at various parts of a quartz cell by a photographic method depending upon the property of the protein to absorb in the ultraviolet. In order to measure the concentration of the protein by means of the density of a photograph obtained by passing light from a mercury arc through the solution, it is necessary that a strong absorption band of the protein be used. Since the protein does not absorb much light of wave-lengths longer than about 2950A, it is necessary that such light be removed by a filter to prevent the light from affecting the photographic plate. A combination of chlorine and bromine filters absorbs most rays longer than 2950A and passes those shorter. Although the filter does not remove the yellow mercury line, this does not affect the photographic plate.

To obtain the 2537A line alone by methods other than the use of special reso-

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[132] Oldenberg, O., *Z. Physik*, 29, 328 (1924).

[133] Svedberg, T., and Nichols, J. B., *J. Am. Chem. Soc.*, 48, 3085 (1926).

nance lamps, it has been proposed to use the halogens at higher concentrations Peskov [184] calculated from their extinction coefficients that the bromine should b about 0.0046 molar and the chlorine 0.176 molar or about 4 atmospheres. Oldenberg [185] proposed to avoid any absorption of the 2537A line by bromine [186] b omitting the latter and employing chlorine at a pressure of 6.5 atmospheres. Suc high-pressure filter cells have been constructed of quartz. The absorption of th chlorine filter has been measured by Villars.[137] Calculations showed the Pesko filter would be the more nearly monochromatic and would transmit about 27 per cen of the light incident at 2537A. Taylor [138] states that filters (not at high pressure) of chlorine gas or of chlorine in carbon tetrachloride show a decreasing absorptio per unit with increasing thickness and that the decrease is not exponential. Th last small per cent of actinic light is difficult to remove.

As a filter for altering the intensity of the 2537A line, Melville and Walls [13] propose sulfur-free carbon tetrachloride mixed with purified hexane or preferably cyclohexane. Such filters show decomposition after 15 minutes.

The mercury arc has another strong line at 3650A. Filters for isolation of thi line have been proposed by Hartmann,[140] Luther and Forbes,[141] Winther,[14] Andrich and Le Blanc,[143] and Buttolph.[144] Absorption data regarding the Luther-Forbes filter (0.78 cm. of a solution containing 0.0785 g. fuchsine S, 0.0164 g methylene blue, 0.0410 g. *p*-nitrosodimethylaniline per liter) and the Winther filte (1 cm. of 0.03-per cent aqueous Diamant Fuchsine) have been given by Gray.[14] The former gave in a 1-cm. layer a maximum transmission of 8 per cent at 3650A In one-fifth strength, 2 cm. transmitted 30 per cent. Acids and alkalies alter absorption by the Luther-Forbes filter, as well as that of the Winther filter. It is th opinion of Potapenko [146] that the most suitable form of light filter for Uviol lamp is a stained gelatin film, which may be prepared by coating glass with a gelati solution containing the desired dye, and after drying, stripping the film so formed A list of dyes for various wave-lengths was given by Miethe and Stenger [147] an by Mannich.[148] Staats [149] has discussed the problem of making monochromati glass filters for the wave-lengths 1014, 578, 546, 436, 405, and 365 mμ of the mercur arc. In each, two components are used, (a) a glass which absorbs with shar cut-off, all radiations of wave-length shorter than the one it is desired to transmi and (b) one with a similar absorption for longer wave-lengths. The ratio of th thicknesses of the two components is specified for each filter. Graphs give the variation in transmission and purity of the transmitted light for each of 15 combinations In some, auxiliary filters are required. Since the characteristics of such filter depend upon the spectral distribution of the source and the sensitivities of the

[184] Peskov, N. P., *Z. wiss. Phot.*, **18**, 235 (1919); *J. Russ. Phys.-Chem. Soc.*, **47**, 918 (1915).

[185] Oldenberg, O., *Z. Physik*, **29**, 328 (1924).

[186] Coehn, A., and Stuckardt, K., *Z physik. Chem*, **91**, 722 (1916).

[137] Villars, D. S., *J. Am. Chem. Soc.*, **48**, 1874 (1926).

[138] Taylor, W., *Nature*, **118**, 697 (1926).

[139] Melville, H. W., and Walls, H. J., *Trans. Faraday Soc.*, **29**, 1255 (1933).

[140] Hartmann, J., *Z. wiss. Phot.*, **1**, 259 (1903).

[141] Luther, R., and Forbes, G. S., *J. Am. Chem Soc.*, **31**, 770 (1909).

[142] Winther, C., *Z. Elektrochem.*, **19**, 389 (1913), for filters for other lines, (5790, 5460, 4360, 4050, and 3130A), see Winther, C., *Ibid.*, **43**, 691 (1937).

[143] Andrich, K., and Le Blanc, M., *Z. wiss. Phot.*, **15**, 187 (1915).

[144] Buttolph, L. J., *J. Opt. Soc. Am.*, **6**, 1066 (1922).

[145] Gray, L. T. M., *J. Phys. Chem.*, **31**, 1732 (1927).

[146] Potapenko, G., *Z. wiss. Phot.*, **18**, 238; *Chem. Abs.*, **14**, 699 (1920).

[147] Miethe, A., and Stenger, E., *Z. wiss. Phot.*, **19**, 57 (1919); *J. Soc. Chem. Ind.*, **39**, 313A (1920).

[148] Mannich, C., *Chem. Ztg.*, **33**, 1167 (1909).

[149] Staats, E. M., *J. Opt. Soc. Am.*, **28**, 112 (1938).

receivers, they apply only to a specified source (H-3 capillary high-pressure mercury arc) and specified receivers.

When it is desired to remove infrared rays to prevent their possible effects on the temperature of solutions undergoing photochemical reactions, water is employed as a filter in a quartz cell. A 1-cm. thickness transmits 58 per cent at 9450A and 14 per cent at 11,900A.[150] Coblentz has suggested filters to absorb the infrared completely.[151] Sodium, potassium, ammonium and thallium chlorides act as selective filters in the region 40-140µ.[152] A filter solution which transmits the visible rays and absorbs ultraviolet rays shorter than about 4000A may be made from quinine sulfate.[153] Clarke [154] describes a light filter for absorbing blue-violet and ultraviolet rays. It is formed of gelatin or other light-transmitting material containing a salt of glucose-phenylosazone-*p,p'*-dicarboxylic acid. An acid which in 0.01 per cent solution (2-cm. layer) absorbs ultraviolet and passes most of the visible rays is made by Suzuki and Sakurai [155] by condensing dextrose or invert sugar with phenylhydrazine-*p*-sulfonic acid in the presence of sodium or potassium acetate at 100°C. Used in a gelatin filter, 2 gms. per sq. meter, this filter completely absorbs the ultraviolet. It is claimed that the insoluble basic lead salt of the acid provides an ultraviolet-ray proof paint. A colorless pyrene compound, such as pyrene-3,5,8,10-tetrasulfonic acid, with steep absorption curve at about 4100A, has been proposed as a filter ingredient for removing ultraviolet rays by Wiegand, Merkel and Tietze.[156] Wilmanns, Dieterle and Weichmann [157] suggest for this purpose cyanines containing two benzoxazole rings, or one such ring and one benzothiazole ring, or a benzoxazole and a thiazoline ring, or a benzothiazole and thiazoline ring, bound in the 2,2'-positions to the nitrogen atom by a carbon atom.

Bakelite panels 0.5 mm. thick transmit 30 per cent at 3126A, 3 per cent at 2800A, and none at 2750A, the resin turning yellow.[158] Zernik [159] proposes hydroxylquinoline sulfonic acids and their alkyl or aryl ethers as colorless light filters for ultraviolet rays.

A filter for wave-lengths between 2900 and 3200A may comprise a film of trihydroxytriethylamine salicylate or *o*-cresotate or other compound of the formula $HO—R—COONH(C_6H_4OH)_3$, where R is a benzene or naphthalene ring and the hydroxyl group of the nucleus and the carboxyl group are in ortho-relation.[160]

A series of long-wave-pass filters has been described by Schneider and Sperti.[161] The shortest mercury arc line which appears on a photospectrogram through 2 cm. of each filter solution following an exposure of 5 seconds (Gaertner quartz spectrograph) is given in Table 16. The line of next shorter wave-length in each case does not appear with an exposure of 60 seconds. The figures given in the second column are the number of cubic centimeters of water in which one gram of substance is dissolved.

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[150] Nichols, E. F., *Phys. Rev.*, **1**, 13 (1893).

[151] Coblentz, W. W., *Bur. Standards Bull.*, **7**, 655 (1911); **9**, 110 (1913).

[152] Hirsekorn, H. G., *Ann. Physik*, **6**, 985 (1930).

[153] Weyl, Th., "Die Methoden der Organischen Chemie," Vol. **1**, p. 313, Leipzig, G. Thieme, (1909).

[154] Clarke, H. T., U. S. P. 1,293,039, Feb. 4, 1919.

[155] Suzuki, T., and Sakurai, S., U. S P. 1,684,562, Sept. 18, 1932, to Zaidan Hojin Rikagaku Kenkyujo; *Chem. Abs.*, **22**, 4735 (1928). British P. 242,721, Aug 18, 1924.

[156] Wiegand, C., Merkel, E, and Tietze, E, U. S. P. 2,122,828, July 5, 1938, *Chem. Abs.*, **32**, 6509 (1938).

[157] Wilmanns, G., Dieterle, W., and Weichmann, H. K, German P. 654,900, Jan. 4, 1938; *Chem. Abs.*, **32**, 3268 (1938).

[158] Risler, J., *Compt. rend.*, **181**, 782 (1925).

[159] Zernik, F., U. S. P. 1,688,259 Oct. 16, 1928; *Brit. Chem Abs.*, **B**, 528 (1929).

[160] Stockelbach, F. E., U. S. P. 2,128,334, Aug. 30, 1938; *Chem. Abs.*, **32**, 8274 (1938).

[161] Schneider, H., and Sperti, G., *Bull. Basic Sci. Research*, **1**, 9 (1926); Goode, G. P., *Ibid.*, **5**, 41 (1933).

Table 16.—Transmission of Ultraviolet Rays by Filters.

Salt	Dilution	Wave-length Limit, A
Ammonium Sulfate	Concentrated	2030
Strontium Chloride	Concentrated	2120
Calcium Chloride	2	2220
Acetic Acid	500	2250
	50	2300
	20	2370
Lead Acetate	(0.28 g. per l.)	2380
	1000	2450
	600	2480
	200	2570
Copper Sulfate	100	2570
Lead Acetate	(15 g. per l.)	2650
	40	2680
	20	2750
Copper Sulfate	40	2880
	25	2960
	3	3130
Cupric Chloride	20	3340

In the preparation of these filters, no attention was paid to the purity or hydration of the materials. Instead, after preparation, the filters were tested spectrographically and adjusted by the addition of water or concentrated salt solution. A semi-commercial scale apparatus in which these filters may be employed for the irradiation of large areas of solutions or liquids of various kinds has been described. (Figure 91.)[162]

Two Hanovia 500-watt quartz mercury arc burners, operated at 135-145 volts a.c. are housed in two separate square metal shields equipped with air-cooling louvres. On the housing of each burner are mounted three filter cells, the frames of which are of chromium-plated brass, 10 by 17.5 cm., equipped with large quartz filter plates 2 cm. apart. The quartz plates are sealed to the cell frames with picein wax. The joints on the side next to the lamp are cooled by water which flows through the hollow section of the filter frame. The filter solutions are kept in five-gallon glass storage bottles in the top of the unit. All piping and valves in the filter feed and drain lines are either copper, brass, or chromium-plated brass. The filter solutions are forced through the lines by air pressure, maintained at ten pounds by a regulator. The flow is made visible by a drip cup in the drain line mounted on the front of the unit; its rate is adjusted to change the solution in each cell every fifteen minutes. Six different filter solutions and distilled water are available for each lamp at any time by opening the proper line valves on the front panel. Nitrogen and ice water outlets are mounted on the unit so that a nitrogen atmosphere and cooling may be applied continuously to the material irradiated. Motor-driven rotating and stirring devices are built into each lamp housing. It is possible to irradiate oils in thin films in large rotating cylinders, solutions in rotating test tubes, and liquids in various types of cells equipped with stirrers. The distance from the burners to the cells is approximately 15 cm. Three experiments, utilizing different filters, may be carried on simultaneously with each lamp, or six with the complete unit.

Withrow[163] describes filters for the region 2900 to 3200A, made of solutions of organic acids adsorbed on regenerated cellulose or impregnated in gelatin sheets, the latter being the stronger and having the smoother surfaces. In each of the

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[162] Goode, G. P., *Bull. Basic Sci. Research*, 5, 39 (1933); U. S. P. 1,966,546-7, July 17, 1934, to General Development Laboratories, Inc.

[163] Withrow, R., *Bull. Basic Sci. Research*, 3, 82 (1931); U. S. P. 1,938,734, Dec. 12, 1933, to General Development Laboratories, Inc.

FIGURE 91. Ultraviolet Irradiation Unit. (Goode, *Bulletin Basic Science Research*).

three solutions used, the solvent is one liter of water and 125 cc. of glycerin to prevent cracking. No. 1 contains 80 gm. of sodium benzoate, No. 2, 40 gm. of potassium acid phthalate[164] and No. 3, 30 gm. of cinnamic acid and 10 gm. of potassium hydroxide. Sheets of the desired size of No. 600 Du Pont Cellophane are soaked in the desired solution for 12 hours and allowed to dry. In making gelatin filters, powdered gelatin in unspecified quantity is dissolved in the filter solution and the liquid spread on sheets of glass or quartz. The transmission curves of these three filters are given in Figure 92, in which Corex D and Quartz-lite are added for comparison. On intense irradiation, particularly with the shorter wave-lengths, these filters deteriorate, the absorption limit shifting toward longer wave-lengths. For this reason, it is advisable to use these filters in conjunction with a filter of Corex D which absorbs much of the energy in the shorter wave-lengths, the gelatin filters serving to sharpen the absorption limits. Under such conditions, two sheets of No. 1, absorb practically all radiations shorter than the 2890A line, two sheets of No. 2 all beyond the 3130A line and three sheets of No. 3 those beyond the 3340A line.

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[164] Suggested by Saunders, F., *J. Opt. Soc. Am.*, 16, 362 (1928).

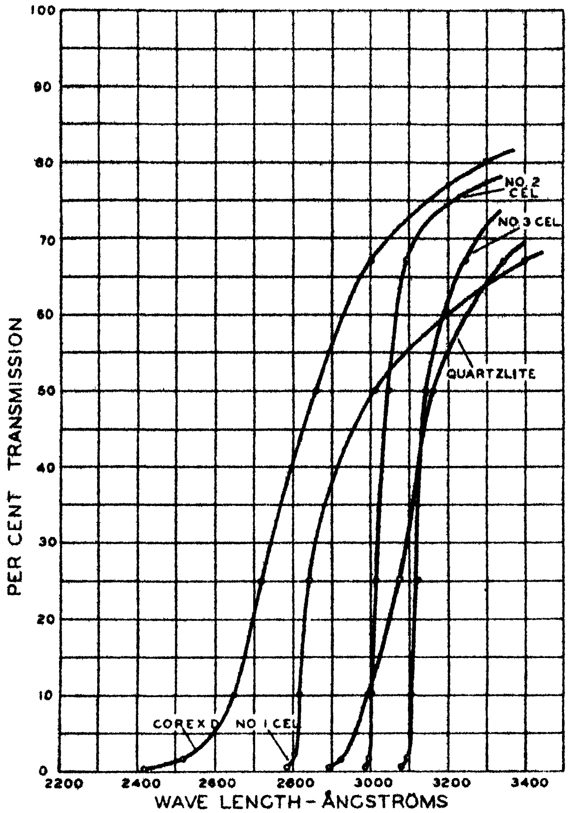

FIGURE 92. Transmission Characteristics of Various Filters (Withrow, *Bull. Basic Science Research*).

Jones[165] described a set of eight filters, only two of which were intended for the ultraviolet region, the others covering the visible and infrared. One ultraviolet filter was made by combining 2 cm. of 10 per cent copper sulfate solution with 3.2 mm. of Corning glass G 586. This filter transmits between 3300 and 4300A with a maximum of 69 per cent at 3800A. At all wave-lengths between 4300 and 12,000A, transmission is less than 0.1 per cent. The other ultraviolet filter combined a 1 cm. layer of a 50 per cent aqueous solution of $NiSO_4.7H_2O$ with 3.2 mm. of Corning glass G 986A. It transmits between 2600 and 3600A, with a maximum of 50 per cent at 3100A. By adding 1 cm. of 2 per cent $CuSO_4.5H_2O$, all wave-lengths shorter than 3100A can be absorbed. Bhagwat[166] has determined the transmission of solutions of nickel salts. Combinations of these salts with cobalt salts transmit only in the ultraviolet, a mixture of 3.66*M* cobalt chloride and 2.08*M* nickel nitrate transmitting 3307-3598A. The cobalt salt alone transmits the 2618-4063 and 7100-7600A regions.

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[165] Jones, L. A., *J. Opt. Soc. Am.*, **16,** 259 (1928); *J. Nutrition*, **2,** 111 (1929); *Chem. Abs.*, **24,** 1889 (1930).

[166] Bhagwat, W. V., *J. Indian Chem. Soc.*, **11,** 5 (1934); *Bull. Acad. Sci. United Provinces Agra Oudh*, **2,** 67 (1932); *Chem. Abs.*, **29,** 7192 (1935).

Another list of ultraviolet filters for the mercury lamp, most of which also remove the infrared, has been proposed by Bowen,[167] who employs the filters in round flasks which serve as condensers, increasing the light intensity. One flask a few centimeters from the lamp gives approximately parallel light. Two flasks almost in contact and with one nearly touching the burner, give more intense light converging to an image about 5 cm. beyond the second flask. For the regions (a) the yellow and green lines and (b) blue, violet and 3665A lines, the first flask (glass, 10-12 cm. diameter) contains distilled water and the second, a double-walled Dewar flask, has the inner part filled with water and the 1-cm. space filled with a solution of 60 gm. $CuSO_4 \cdot 5H_2O$, 2 gm. $K_2Cr_2O_7$, 55 cc. of concentrated sulfuric acid and made up to one liter with water. With this arrangement, 3.4 mm. Corning 344 transmits only the 5790 and 5770A lines, and 5 mm. Corning 512 only the green line 5460A. For the region (b), the solution for the outer part of the Dewar flask is 20 gm. $CuSO_4 \cdot 5H_2O$ and 300 cc. aqueous ammonia made to one liter with water. With this solution, 2.5 mm. Corning Noviol A glass transmits only the blue line 4360A, 2 mm. of Corning Noviol 0 and 1 cm. of a carbon tetrachloride solution of iodine (7.5 gm. per liter) transmits only the 4060A line and 2 to 2.5 mm. of Chance's black ultraviolet glass transmits only the line 3665A.

For the ultraviolet region, 10 cm. spherical quartz flasks are used. For the region 3340-2800A, the first flask has a solution of 70 gm. $NiCl_2 \cdot 6H_2O$ and 30 cc. concentrated hydrochloric acid per liter. For the region 2800-2480A, a solution of one-fifth that concentration is employed. These solutions remove the infrared and 4060A lines and greatly reduce the 3665A line. For the 3340A line, the second flask contains uric acid in water saturated at 15°C. For the 3135A line, this flask has a potassium chromate solution made by diluting 5 cc. of a stock solution (3.0 gm. per liter) with 5 cc. of 2*N* sodium hydroxide and 490 cc. of water. The filter is used with a 1-cm. plane quartz cell containing circulated potassium hydrogen phthalate (13 gm. per liter) in water. For the 3135, 3030 and 2970A lines, the second flask contains 60 cc. of a stock solution of Auramine 0 (0.125 gm. per liter) in 440 cc. of water, and is used with 1 cm. of circulating saturated benzoic acid in water. For the 3030 lines (and all shorter ones), the second flask contains water. For the 3030A line, there is used 1 cm. of benzene circulating at the rate of 4 liters per hour; for 2650A, chlorine gas at 760 mm. (3 cm. layer) and a circulating solution of pure benzene in water (1 cm.) (82 cc. of the saturated solution at 15°C. diluted to 100cc.). For the 2750-2480A lines, 3 cm. of chlorine gas at atmospheric pressure is used. For the 2540A line, there is employed in addition to the chlorine filter, 1 cm. of a solution made by diluting 8.6 cc. of a solution of 12.7 gm. iodine and 18 gm. of potassium iodide per liter, to one liter. Transmission data for these filter arrangements are given. Some changes in the list were made subsequently.[168]

Slightly different filters, employing also cobalt sulfate in sodium cinnamate, have been recommended by Bäckström[169] for the medium ultraviolet region. Another series, using cobalt, chromium, copper, manganese and nickel salts has been described by Maddock[170] for isolating nine of the principal bands of the mercury spectrum from 2652 to 5780A, giving transmissions of 7 to 36 per cent. Still others are due to Vaidya,[171] who describes 33 such systems and gives approximate measurements of the energy transmitted by eight of them.

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[167] Bowen, E. J., *J. Chem. Soc.*, 2236 (1932).

[168] Bowen, E. J., *J. Chem. Soc.*, 76 (1935).

[169] Bäckström, H., *Naturwiss.*, 21, 251 (1933).

For isolating for Raman studies the mercury triplet at 4358A, Sannié, Amy and Poremski[172] use a filter solution containing 5 per cent nitrobenzene and 0.01 per cent rhodamine 5G Extra in ethanol. A thickness of 1 cm. gives a transmission of 0.001 for the lines 4046 and 4916 and of 0.95 for the desired triplet. Glass filters for other lines for Raman work have also been described by Amy.[173]

In Raman work, the 4046A line is better absorbed by Noviol A than by sodium nitrite solution, which is subject to change.[174]

According to Bhagwat and Dhar[175] the ammonia complex of cupric chloride is a good filter for the region 4000 to 4590A. Cupric chloride with cobaltous chloride is satisfactory for the lines 2961 and 3248-74A.

Mica[176] has occasionally been used as a filter material. Ruby mica absorbs the least; in a 0.03 mm. layer the transparency limit is 2900A. In 0.75 mm., it is 3500A. Green species absorb more strongly, as only traces pass through 0.5 mm. layers. Deep-brown Madagascar mica absorbs totally in 0.1 mm. layers.[177]

Transmission by Clothing. It is of interest to consider the degree to which our clothing prevents access of the ultraviolet to the body. Dozier and Morgan[178] were unable to produce vitamin D in oils by irradiating them through baby flannel, pongee and crepe de Chine, although artificial silk and meadow lane materials transmitted the active rays. The mean interspace between threads and the weight are the important factors.[179] Trotman,[180] who used a light sensitive dyestuff as an indicator of the permeability of the fabric to ultraviolet, was unable to detect any transmission even through viscose, cuprammonium, chardonnet and celanese rayons. Coblentz, Stair and Schoffstall[181] have made physical measurements of the transmission of ultraviolet radiation through various fabrics. Comparing materials having the same weight, practically no difference was found in the amount transmitted through bleached samples of cotton, linen, viscose silk and cellulose acetate silk. Fresh, white natural silk is almost as translucent as bleached cotton, but wool is only half as transparent. In all cases when the fabric is dyed, or slightly yellow with age, the ultraviolet transmission through the thread is greatly decreased. Hence, in comparing dyed fabrics, the one with the largest openings between the threads transmits the most ultraviolet radiation.

Hirst, King and Lambert[182] found every one of over a hundred fabrics to cut off a large proportion of the ultraviolet radiation, the weave and texture being more important than the material of the fiber. For equal thicknesses of material, they believed wool to have on the whole a higher transmissive power than the other fabrics tested. Any kind of dyeing decreases the ultraviolet transmission.

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[170] Maddock, A. J., *J. Sci. Instruments*, **12**, 218 (1935).

[171] Vaidya, B. K., *J. Univ. Bombay*, **3**, Pt. 2, 141 (1934); *Chem. Abs.*, **29**, 6508 (1935).

[172] Sannié, C., Amy, L., and Poremski, V., *Compt. rend.*, **202**, 1042 (1936).

[173] Amy, L., *Documentat. Sci.*, **4**, 97 (1935); *Chem. Zentr.*, **II**, 2848 (1935).

[174] Biquard, D., *Documentat. Sci.*, **5**, 81 (1936); *Chem. Abs.*, **31**, 7758 (1937). See, however, Bayley, P. L., *J. Opt. Soc. Am.*, **27**, 303 (1937).

[175] Bhagwat, W. V., and Dhar, N. R., *J. Phys. Chem.*, **35**, 2383, 2391, 2401 (1931).

[176] Hausmann, W., and Krumpell, O., *Strahlentherapie*, **35**, 387 (1930); Takagi, T., *Ibid.*, **40**, 189 (1931).

[177] Finkelnburg, W., *Naturwiss*, **14**, 919 (1926).

[178] Dozier, C. C., and Morgan, H., *Am. J. Physiol.*, **84**, 603 (1928).

[179] Morgan, H., *Am. J. Physiol.*, **86**, 32 (1928).

[180] Trotman, S. R., *Textile Recorder*, **47**, 63 (1929); *Chem. Abs.*, **23**, 2297 (1929).

[181] Coblentz, W. W., Stair, R., and Schoffstall, C. W., *Bur. Standards J. Research*, **1**, 105 (1928).

[182] Hirst, H. R., King, P. E., and Lambert, P. N., *J. Soc. Dyers Colourists*, **44**, 109 (1928); *Chem. Abs.*, **22**, 2061 (1928); Eccles, J., *Silk J.*, **7**, 37 (1931).

Young[183] suggested tracing cloth as a substitute for the more expensive ultraviolet glasses for use in country cottages, chicken farms, etc. This could not be confirmed at the Bureau of Standards. The total ultraviolet of wave-lengths 2500-3100 diffusely transmitted through a new sample of tracing cloth amounted to about 26 per cent before wetting and 14 per cent after removing the sizing and drying the cloth. Balloon fabric transmits 21, batiste 16, and nainsook 31 per cent.

Physical Methods for Isolating Lines or Wave-Length Bands

Unique among filters employing physical principles is that of Christiansen, which acts on[184] the principle that a suspension of a finely divided solid in a liquid transmits only radiations of the wave-length at which the refractive index of the solid is the same as that of the liquid. While such filters have frequently been used in the visible region, the principle has only recently been extended to the ultraviolet.[185] A solution of 56 per cent benzene and 44 per cent ethanol containing amorphous silica at 20°C. transmits at 3600A. Such filters are very sensitive to temperature changes. Andrews[186] furnishes details of an apparatus for separating visible from ultraviolet light, which depends upon the fact that the visible rays are less refracted by a lens than is the ultraviolet radiation. Figure 93 diagrammatically shows the design of the apparatus. A is a source of visible light, also producing ultraviolet rays. B is a quartz lens. D is a thin sheet of metal pierced with a pinhole at C, the diaphragm being so placed that the pinhole is in the exact mean focus of the visible rays. F is a small metal disk and G is a screen. A front view of the screen is shown at H. The operation of this instrument is based on the fact that the mean focus of the visible light is located at a measurable distance beyond the mean focus of the invisible rays owing to the greater refrangibility of the latter over that of the former. If, therefore, the diaphragm D is carefully adjusted so as to bring the pinhole C into the exact mean focus of the ultraviolet rays, the rays of the latter will pass through the pinhole and spread out again on the other side of the diaphragm. The mean focus of the visible light being some distance beyond the pinhole, its rays will be largely intercepted by the diaphragm, and through the pinhole only a few of the nearly parallel rays of visible light will pass. In operation, if the screen H is made of non-fluorescent material, there will appear on it only the small illumi-

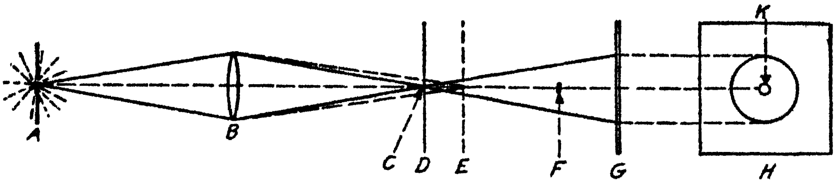

Figure 93. Diagram Showing Principle of Andrew's Separator.

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[183] Young, C. H., *Nature*, **123**, 47 (1929).

[184] See Holst, G., *Z. wiss. Phot.*, **36**, 145 (1937); *Brit. Chem. Abs.*, **B**, 479 (1937).

[185] Kohn, H., and v. Fragstein, K., *Physik. Z.*, **33**, 929 (1932); Ahier, G., *Compt. rend.*, **205**, 37 (1937).

[186] Andrews, W. S., *Gen. Electric Review*, 817 (1917).

nated spot K, but if it be coated with a fluorescent substance, such as powdered willemite, this small luminous spot will be surrounded by a disk of bright green light produced by the fluorescence of the willemite excited by the circular field of invisible ultraviolet rays. Should it be found desirable to cut out the spot of visible light, the small metal disk F can be set up in such a position as to cast its shadow over the spot K and so transform it from a bright spot to a dark one, leaving the disk of green fluorescent light otherwise unchanged.

The method has been extended by Terenin[187] to the separation of various ultraviolet regions. Forbes, Heidt and Spooner[188] prefer it to the monochromator for the aluminum lines around 1940A and the zinc lines near 2030-2014A.

Another way of getting a monochromatic radiation is to employ the rays given out by cold mercury vapor when transversely illuminated by a mercury vapor arc. This radiation is about one-fortieth as intense as the 2537A line of the original source, but offers some possibilities for photochemical work.[189] Very low voltage arcs also deliver monochromatic radiation in the resonance lines, but this radiation is of low intensity.[190]

By far the most generally used optical method employs a prism monochromator. Light from the source passes through a slit to a prism (a collimating lens may be added) and after passing a lens emerges through an exit slit, which is narrow enough to exclude all but the desired wave-length region. This slit is also movable so that any desired wave-length range may be isolated. Any such instrument must, however, represent a compromise between monochromatic purity and loss of intensity. For greater intensities, monochromators are best employed with the constricted mercury arc as source. Details are to be found in the catalogs of instrument makers or in textbooks on optical instruments. Many photochemists design and build their own monochromators; valuable suggestions regarding such instruments and the optical losses they involve have been given by Forbes.[191] Details have been given by Heidt and Daniels[192] regarding laboratory-built instruments and by Kurtz[193] regarding a commercial type. Reflection losses in the Hilger monochromator have been studied by Ridyard and Style.[194] Granath[195] calculates that in the Hilger E 31 quartz spectrograph, the absorption at 1860A by the quartz is 50 per cent and by the air 17 per cent. At 1900A, the values are 31 per cent and 3 per cent, at 2000A, 23 per cent and 1 per cent and at 2100A, 16 per cent and 0.5 per cent, respectively. Forsythe and Barnes[196] have described a quartz monochromator especially intended for studying the intensity of the radiation in the ultraviolet spectrum from various sources.[197]

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[187] Terenin, A., *Z. Physik*, **31**, 33 (1925).

[188] Forbes, G. S., Heidt, L. J., and Spooner, L. W., *Rev. Sci. Instruments*, **5**, 253 (1934).

[189] Wood, R. W., *Physik. Z.*, **13**, 353 (1912); Cario, G., and Franck, J., *Z. Physik*, **17**, 205 (1923)

[190] Foote, P. D., and Meggers, W. F., *Bur. Standards Bull.*, **16**, 317 (1920).

[191] Forbes, G. S., *J. Phys. Chem.*, **32**, 496 (1928).

[192] Heidt, L. J., and Daniels, F., *J. Am. Chem. Soc.*, **54**, 2384 (1932); see also Benford, F., *J. Opt. Soc. Am.*, **26**, 99 (1936).

[193] Kurtz, H. F., *J. Opt. Soc. Am.*, **13**, 495 (1926); see also Villars, D. S, *J. Am. Chem. Soc.*, **49**, 326 (1927).

[194] Ridyard, H. N., and Style, D. W. G., *J. Phys. Chem.*, **32**, 861 (1928).

[195] Granath, L. P., *Phys. Rev.*, **34**, 1045 (1929).

[196] Forsythe, W. E., and Barnes, B. T., *Rev. Sci. Instruments*, **1**, 569 (1930).

[197] See also Fortrat, R., *Rev. optique*, **16**, 386 (1937); Pelton, M. O., *J. Sci. Instruments*, **15**, 169 (1938); Perry, J. W., *Proc. Phys Soc.* (London), **50**, 265 (1938).

Chapter 11

The Sun as a Source of Ultraviolet Radiations

The discussion of filters in the preceding chapter paves the way for a consideration of the amount and quality of the ultraviolet energy available on the earth's surface, since a large portion of the energy emitted by the sun is absorbed in the earth's atmosphere. Only about 70 to 78 per cent of the sun's total radiant energy of all wave-lengths which strikes the upper atmosphere gets through to sea level when the sun is at the zenith and the air is free from dust and clouds.[1]

Astrophysical evidence indicates that the past billion years is only a small fraction of the period since the sun began to shine. In the past billion years, it has emitted 1.20×10^{50} ergs of energy (3.79×10^{33} ergs per second times 10^7 seconds per year $\times 10^9$ years). This is more than three billion billion billion billion kilowatt-hours. Expressed per gram of the sun's mass (1.983×10^{33} grams), the radiation per year is 6.05×10^7 ergs (1.44 calories); in a billion years at this rate, the radiation has amounted to 6.05×10^{16} ergs per gram, a lower limit.

It is believed that the whole ball of the sun is composed of hot gases, increasing inward in temperature and density. We see only the surface layer of gases—only down to where the density is a thousandth part of an atmosphere. This visible skin—photosphere—contains only as much mass as would a layer of a few feet of atmospheric air around the sun, far too little to produce the intense energy radiation. This must, therefore, be produced below the photosphere and flow toward the surface, which itself has a temperature of about 6000°K.

Many suggestions have been made as to the nature of the processes producing this energy; most of those based upon processes experimentally familiar have been found quantitatively inadequate. Recently, astronomers such as Eddington, have adopted the principle of Einstein that mass is in some way equivalent to energy and have built upon this models to describe the solar, or more generally, stellar radiation processes.

This principle states that a loss of m units of mass corresponds to the liberation of mc^2 units of energy, where c is the velocity of light. This constitutional energy is 8.99×10^{20} ergs per gram, about 15,000 times the estimated radiation per gram of the sun's mass during the past billion years. The Einstein principle of the equivalence of energy and mass would imply that the sun is losing 4,660,000 tons as energy per second, the earth receiving four pounds and three ounces as energy per second.[2]

In Eddington's theory, the material throughout the sun is in the state of a nearly perfect gas, the density increasing toward the center at such a rate that at the center it is about 54 times the mean density (1.41 grams per cubic centimeter). This would make the central density more than three times greater than that of platinum. The gas at the center of the model sun is assumed to be under a pressure of more than a billion atmospheres and at a temperature of nearly 40 million degrees K. At such temperatures, it is believed that the shells of electrons are torn off from the atoms, leaving them stripped so that the kernels which remain are small enough for the gas to behave as such despite its high density.

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[1] Stewart, J. Q., [*J Frank. Inst*, **204**, 438 (1927)] has given an interesting general account of the theories of the origin of stellar energy, from which much of the information in these paragraphs has been derived.

[2] Discussion by Eddington, A. S., *Nature*, **117**, Supplement to May 1 (1926); see, however, Jeans, Sir J., *Nature*, **117**, 689 (1926); Menzel, D. H., *Science*, **65**, 431 (1927); Nernst, W., *J. Frank. Inst.*, **206**, 135 (1928). See also, Landau, L., *Compt. rend. acad. sci. U.R.S.S.*, **17**, 305 (1937); *Chem. Abs.*, **32**, 2426 (1938).

Although considerations such as these are highly speculative, they may serve to afford some conception of the nature of the problems involved.

In the spectra of the sun about 60 elements have been identified.[3] Russell[4] has surveyed and discussed the evidence regarding the relative abundance of the elements in the sun's atmosphere. Sodium, magnesium, silicon, potassium, calcium and iron form 95 per cent of the whole mass. Elements of even atomic numbers are ten times as abundant as those of odd atomic numbers. The metals from sodium to zinc are far more common than any others. Compounds are present only in small amounts, cyanogen being rarer than scandium. The presence of boron and phosphorus has been much discussed. The estimated temperature of the reversing layer is 5600° and the pressure at its base is 0.005 atmosphere. It appears to contain 60 parts of hydrogen (by volume), two of helium, two of oxygen, one part of metallic vapor and 0.8 of free electrons. The temperature of the sun spots is close to 4900° absolute.[5]

Effects of the Earth's Atmosphere on Solar Radiation. Most of the lines which have been studied in deriving information on solar radiation have been located in the infrared and visible regions. Only a small part of the ultraviolet adjacent to the visible has been included. This is because the earth's atmosphere absorbs the shorter ultraviolet radiations; according to Lyman, the physicist Cornu found the spectrum of the sun to terminate quite abruptly at about 3000A. Our knowledge of the actual ultraviolet output of the sun, or of the amount of ultraviolet energy which reaches the outer layers of the earth's atmosphere is, therefore, limited because of absorption of ultraviolet within the atmosphere. It has been necessary to depend upon indirect methods, such as a consideration of the nature of the absorbing substance or substances and their distribution in the atmosphere in drawing conclusions as to the probable amounts of ultraviolet reaching the outer atmosphere. The most extensive estimates of the energy distribution outside the atmosphere have been made by Abbot[6] for the region 4000A, and by Fabry and Buisson for shorter wave-lengths.[7] The way in which this energy distribution is computed is about as follows: A series of observations is made of the normal incident energy at various times throughout the day. At these different times the rays pass through different lengths (or masses) of atmosphere. A vertical path gives an "air mass" of one. For variations from the vertical, the "air mass" varies as the secant of the angle. By graphical methods, it is possible to obtain from a series of intensity observations with different "air masses" an extrapolated value for an "air mass" of zero which represents the sun's energy before it is filtered by the atmosphere. Thus at 3100A the transmission for "air mass" of 1 is 0.1, and for "air mass" of 2, 0.01 (8 A.M. or 4 P.M.) and at "air mass" of 3 it is only one part in a thousand.[8] During the stratosphere flight of the Explorer II to 72,395 feet, the total ultraviolet increased not over 4 per cent.[9]

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[3] St. John, C. E., *Proc. Nat. Acad. Sci.*, **15**, 789 (1929); *Astrophys. J.*, **70**, 160 (1930); Dingle, H., in article "Sun" in *Encyclopedia Brittanica*, 14th ed.

[4] Russell, H. N., *Astrophys. J.*, **70**, 11 (1929).

[5] Richardson, R. S., *Astrophys. J.*, **73**, 216 (1931).

[6] Abbot, C. G., *Smithsonian Miscellaneous Collections*, **74**, 15 (1923); *Annals Astrophysical Observatory*, **2**, 112 (1908).

[7] Fabry, C., and Buisson, H., *Compt. rend.*, **175**, 156 (1922); *Astrophys. J.*, **54**, 297 (1921).

From the standpoint of the biologist, the absorption of radiations of the shorter ultraviolet rays by the atmosphere is of the greatest importance. It is shown in Chapter 35 that ultraviolet rays shorter than about 2950A are lethal to bacteria and destructive to living cells. Life, as we know it, could not exist on the earth if the absorption of these shorter rays in the atmosphere did not occur.

It is, therefore, interesting to determine which component of the atmosphere absorbs these rays. Both oxygen and nitrogen absorb strongly only rays of very much shorter wave-length (1850A and less than 1250A, respectively). Accurate data on the absorption by oxygen in the region 1850 to 2300A have been determined by Granath.[10] Earlier important observations were due to Fabry and Buisson,[11] Ladenburg and Lehmann,[12] and Hallwachs.[13] That the absorbing component for bactericidal radiations is ozone has been known for many years, Hartley having been credited with first suggesting it.[14] The origin of ozone in the upper atmosphere is still, however, an unsolved problem, despite a considerable amount of work.[15] According to Fabry,[16] a thickness of ozone of about 3 mm. at normal temperature and pressure would account for the observed absorption. This was calculated from absorption measurements of known concentrations of ozone and of varying thicknesses of the absorbing layer of the earth's atmosphere. Subsequently, a number of papers have been devoted to the distribution of ozone in the atmosphere.

Probably the best opportunity for accurate studies was afforded by the stratosphere flights of the Explorers I and II. These indicated little ozone up to 52,000 feet. Above this, the concentration of ozone increased rather rapidly and at 72,000 feet nearly 25 per cent of the total quantity of ozone lay below the level of the balloon. In the summer flight of 1934, the ozone was equivalent to 2.5 mm. and in the November flight of 1935 to 1.9 mm.[17]

Nitric acid occurs in the atmosphere, more at high than at low altitudes.[18] It has been suggested that the nitrates and nitrites present in the atmosphere are derived from the photochemical oxidation of ammonia.[19] Vorländer and Gohdes[20] find moist air to contain oxides of nitrogen to the extent of $15\text{-}30 \times 10^{-6}$ gm. per cubic meter of N_2O_3. Irradiation with ultraviolet increases this from ten to a hundred times. Ammonia may be decomposed into nitrogen and hydrogen in the stratosphere.[21] Formaldehyde may also be present in air since it may be detected in rainwater. The amount therein is not increased by lightning, but is greater when the rainfall has been preceded by some sunny days. Dhar and Ram[22] suggest that formaldehyde may be produced from carbon dioxide and water by radiation of wave-length 2550A, at altitudes where this radiation has not all been absorbed by the ozone layer.

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[8] Gordon, N. T., and Benford, F., *Gen Electric Review,* **33,** 283 (1930).

[9] Teele, R. P, *National Geographic Society, Stratosphere Series,* No. 2, 133 (1936).

[10] Granath, L. P., *Phys. Rev* , **34,** 1045 (1929).

[11] Fabry, C., and Buisson, H., *Compt rend.,* **156,** 782 (1913).

[12] Ladenburg, E , and Lehmann, E , *Ber. deutsche physik. Ges.,* **4,** 125 (1906).

[13] Hallwachs, W., *Ann. Physik,* **30,** 602 (1909).

[14] Hartley, W. N., *J. Chem. Phys.,* 111 (1881), cited by O'Brien, B., *National Geographic Society, Stratosphere Series,* No. 2, 49 (1936). For recent observations, Dejardin, G., and Arnulf, A., *Compt. rend ,* **205,** 1000 (1937); Vassy, F , *Ann. phys.,* **8,** 679 (1937).

[15] Rayleigh, Lord, *Science,* **70,** 83 (1929); Rosseland, S., *Nature,* **123,** 761 (1929); Ångström, A., *Gerland's Beitr. z. Geophysik,* 21, 2, 145 (1929); Dobson, G. M. B., Harrison, D. N., and Lawrence, J., *Proc. Roy. Soc.,* **114A,** 521 (1927); Dauvillier, A., *Compt rend.* **197,** 1339 (1933); Barbier, D., Chalonge, D., and Vassy, E., *Compt. rend.,* **201,** 787 (1935); Fowle, F. E., *J. Terrestrial Magnetism and Atm. Elec.,* **33,** 151 (1928); Dobson, G. M B , Kimball, H., and Kidson, E., *Proc. Roy. Soc.,* **129A,** 411 (1930); Wulf, O. R., *Phil. Mag* , **17,** 251 (1934); *J. Opt. Soc. Am.,* **25,** 231 (1935); Harteck, P., *Naturwiss.,* **19,** 858 (1931); Mecke, R , *Z. physik. Chem. Bodenstein Festschrift,* 329 (1931); Saha, M. N., *Proc. Roy. Soc.* **A160,** 155 (1937).

[16] Fabry, C., *J. Math. Physics,* **4,** 1 (1925); Cabannes, J., and Dufay, J., *J. Phys. Radium,* **7,** 257 (1926).

[17] O'Brien, B., *National Geographic Society, Stratosphere Series,* No. 2 (1936). Compare Regener, V. H., *Z. Physik,* **109,** 642 (1938). A recent theoretical calculation of the vertical distribution of ozone is due to Wulf, O. R., and Deming, L. S., *Terr. Mag.,* **41,** 299 (1936).

[18] Rao, G. G., and Dhar, N. R., *Z. anorg. allgem. Chem.,* **199,** 422 (1931).

[19] Rao, G. G., *Bull. Acad. Sci., United Provinces Agra Oudh Allahabad, India,* **1,** 82 (1931); *Chem. Abs.,* **26,** 5849 (1932).

[20] Vorländer, D., and Gohdes, W., *Ber.,* **64B,** 1776 (1931).

Suspended ultramicroscopic particles, partly consisting of ammonium nitrite and nitrate and sodium chloride and perchlorate, cause a scattering of radiations, greater at altitudes above those where rain exerts a cleansing effect. Duclaux[23] believes that this may play some part in causing the disappearance of the solar spectrum beyond the ozone bands, and that absorption by oxygen in the short wave region may not wholly account for it.

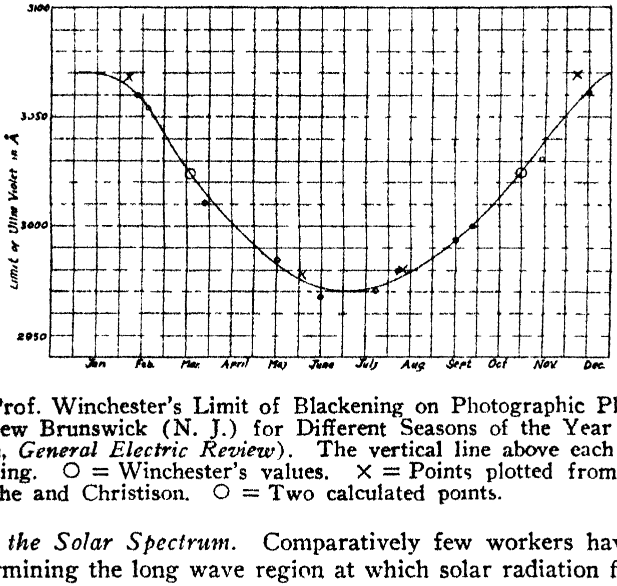

FIGURE 94. Prof. Winchester's Limit of Blackening on Photographic Plates for North Sky at New Brunswick (N. J.) for Different Seasons of the Year (Forsythe and Christison, *General Electric Review*). The vertical line above each month denotes its beginning. ○ = Winchester's values. × = Points plotted from data in paper of Forsythe and Christison. ○ = Two calculated points.

Limits of the Solar Spectrum. Comparatively few workers have been interested in determining the long wave region at which solar radiation first penetrates to the earth. Adel, Slipher and Barker[24] place it at 13.5μ and attribute it mainly to vibration spectra of carbon dioxide and to a lesser extent to ozone. Beyond 17μ there is also absorption by water vapor, the effect of which is also observed in the red region of the visible, according to Beletskii.[25] The regions 8-9 and 10-12μ have high transparency. This radiation in the remote infrared is, however, insignificant in amount; Coblentz and Kahler[26] have stated that but little radiation of wave-lengths greater than 2μ is transmitted by the earth's atmosphere. On some days the infrared energy component from about 2 to 3μ to the limit of the visible may be larger than the visible component. On clear days the two components may be about equal or the visible one may exceed the infrared.

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[21] Matignon, C., *Chimie et Industrie*, Special No. 328, September, 1925.

[22] Dhar, N. R., and Ram, A., *Nature*, **132**, 819 (1933).

[23] Duclaux, J., *J. phys. Radium*, **4**, 625 (1933).

[24] Adel, A., Slipher, V. M., and Barker, E. F., *Phys. Rev.*, **47**, 251, 580 (1935).

[25] Beletskii, F. A., *Zhur. Geofiz.*, **6**, 64 (1936); *Chem. Abs.*, **31**, 3383 (1937).

There have been many determinations of the short-wave length limit since the time of Cornu, but his value of 3000A holds fairly well. The exact value varies greatly with seasonal, altitudinal and other influences. Coblentz and Kahler believed that radiations less than 3000A, if present, amount to less than 5 per cent (20 per cent in the mercury arc) of the total ultraviolet component. Others have stated the limit as 2900A or 2845A. Its variation at Davos in the Swiss Alps has been widely quoted.[27] From December to February, it was 3120A, September to November, 3080A, March to May, 3010A, June to August, 2962A.[28] Fabry and Buisson [29] showed that the amount of energy of wave-length 2900A that reaches the earth's surface is only one-millionth that for 3140A, and even for the larger value the intensity is small. Winchester has given an experimental curve (Figure 94) showing the wave-length limit at New Brunswick, N. J., as detected by the blackening of photographic plates exposed to the north sky at various times of the year. The shortest wave-length found was 2968A on June 1.[30]

Amounts and Distribution of Solar Ultraviolet

Coblentz and Kahler [31] state that the maximum normal solar radiation at perpendicular incidence varies from 1.37 gram calories per minute per square centimeter in January at Washington to 1.5 in May and September. The average seasonal intensity for three hours at noon may be taken as 1.2 gram calories per square centimeter per minute. The total radiation on a horizontal surface, with a clear sky, varies from 0.77 gram calories per minute in December to 1.55 in June. Clouds nearly in line with the sun, but not obscuring it, increase the radiation by about 0.15 gram calories. Otherwise expressed, the maximum radiation that can be received normal to the incident energy is 106 milliwatts per square centimeter.[32] Of the total radiation, only one or two per cent is in the ultraviolet with wave-lengths less than 3889A and more usually may be about half this, while in the case of the quartz mercury arc it may be 30 per cent. Coblentz and Stair [33] found that the upper limit of the total ultraviolet radiation of wave-lengths less than 3100A is less than 0.004 gram calories per square centimeter per minute at sea-level. It cannot exceed 0.3 per cent of the total incident radiation or approximately 300 microwatts per square centimeter Recently, Coblentz believed this figure should be reduced to less than 100 microwatts per square centimeter.[34] Luckiesh [35] concludes that the best midsummer sunlight supplies not less than 25 microwatts per square centimeter, with a probable value of 40 microwatts per square centimeter, of ultraviolet energy shorter than 3100A.

With the growing appreciation of the rickets-preventing value of the radiations between about 3150 and 2900A, there have appeared a great number of studies of the intensity of the available energy in this region and its seasonal, meteorological, altitudinal and other variations.[36] Especial attention has been

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[26] Coblentz, W. W., and Kahler, H., *Sci. Papers Bur. Standards,* No. 378 (1920).

[27] Dorno, C., *Strahlentherapie,* **31,** 341 (1929); Kiepenhauer, K. O., *Naturwiss.,* **25,** 669 (1937).

[28] Cited by Price, W. A., *Ind. Eng. Chem.,* **18,** 679 (1926).

[29] Cited by Forsythe, W. E., and Christison, F., *Gen. Elec. Rev.,* **32,** 664 (1929).

[30] Curve reproduced by Forsythe, W. E., and Christison, F., *Gen. Elec. Rev.,* **32,** 667 (1929).

[31] Coblentz, W. W., and Kahler, H., *Sci. Paper* 378, *U. S. Bureau of Standards,* 1920.

[32] Gordon, N. T., and Benford, F., *Gen. Elec. Rev.,* **33,** 283 (1930).

[33] Coblentz, W. W., and Stair, R., *Bureau Standards J. Res.,* **3,** 629 (1929).

[34] Coblentz, W. W., *Trans. Illum. Eng. Soc.,* **26,** 574 (1931).

[35] Luckiesh, M., "Artificial Sunlight," Van Nostrand, 1920, cited by Coblentz, W. W.; see also Forsythe, W. E., and Christison, F., *J. Opt. Soc. Am.,* **20,** 396 (1930).

[36] Hill, G. L., *Proc. Roy. Soc.,* **102B,** 119 (1927).

devoted to the effects of dust and smoke in lowering the biologically valuable rays.[37] Ashworth[38] considers the effects of winds from towns.

Forsythe and Christison[39] calculated from Abbot's data on the distribution of energy in solar radiations, curves of the transmission of the atmosphere for several wave-length regions, giving the per cents of total radiation and their amounts in milliwatts per square centimeter at Cleveland, Ohio for a horizontal surface, *i.e.*, corrected for the sun's distance from the zenith (Table 17). It must be noted that these are calculated values, rather than the direct results of actual measurements. The values are in fair agreement with similar calculations by Holladay[40] based upon the assumption that the sun radiates as a black body at 6000°K. The paper of Forsythe and Christison also contains theoretical curves showing the variation of energy below 3250 and below 3100A per square centimeter at Cleveland at various times of day during the winter and summer solstices and the spring and fall equinoxes. There is also given a curve for the variation of intensity of wave-lengths less than 3100A at noon throughout the year at Cleveland (Figure 95). They concluded it doubtful if any energy in this region is received from the sun in winter at or near a city where the dust and smoke are quite thick. The making of intensity measurements at various wave-

Table 17.—Transmission of Ultraviolet Rays by Atmosphere.

	1 Atmosphere		1.07 Atmosphere June 21		1.5 Atmosphere Feb. 15		2.37 Atmosphere Dec. 21	
Region	%	Milliwatts	%	Milliwatts	%	Milliwatts	%	Milliwatts
0.31-0.29 μ	0.022	0.024	0.019	0.020	0.0063	0.0061	0.00051	0.0004
Below 0.325	0.24	0.26	0.21	0.22	0.11	0.11	0.029	0.023
Below 0.35	1.1	1.17	1.0	1.07	0.64	0.63	0.27	0.22
Below 0.40	3.9	4.22	3.8	3.97	2.8	2.70	1.62	1.3
0.40-0.76 μ	43.7	46.8	43.9	45.8	42.1	40.4	39.1	31.4
Total		107.0		104.5		96.1		80.2

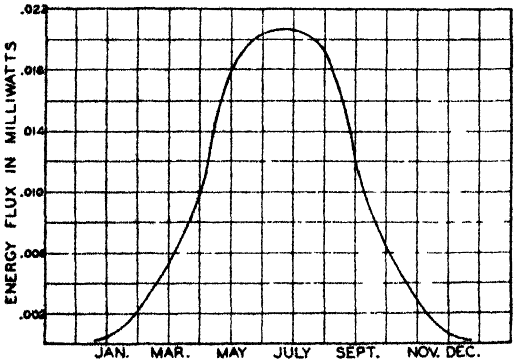

FIGURE 95.

Ultraviolet Energy Below 3100A from the Sun Falling upon a Square Centimeter of the Earth's Surface per Second for the Latitude of Cleveland, Ohio, at Different Times of the Year for 12 Noon. The vertical line above each month denotes its beginning (Forsythe and Christison, *General Electric Review*).

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[37] Bundesen, H. N., Lemon, H. B., Falk, I. S., and Coade, E. N., *J. Am. Med. Assn.*, **89**, 187 (1927).

[38] Ashworth, J. R., *Dept. Sci. Ind. Research, 20th Rept. Investigations of Air Pollution (England)*, 59 (1935); *Chem. Abs.*, **29**, 5560 (1935).

[39] Forsythe, W. F., and Christison, F., *Gen. Elec. Rev.*, **32**, 664 (1929); *J. Opt. Soc. Am.*, **20**, 401 (1930).

[40] Holladay, L. L., *J. Opt. Soc. Am.*, **17**, 329 (1928).

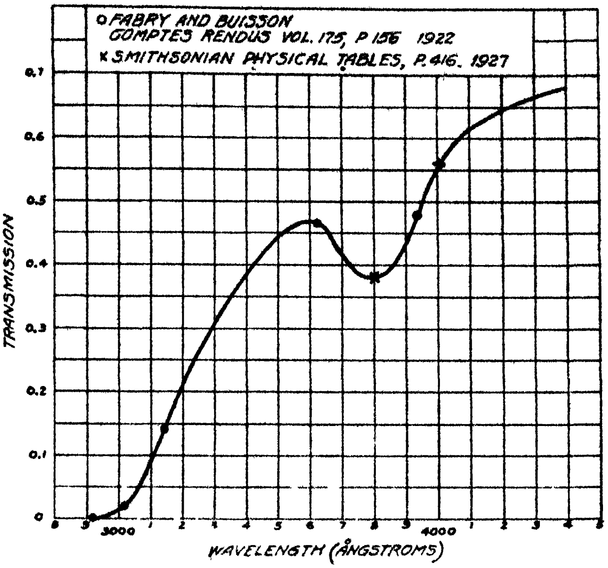

FIGURE 96. Transmission Factors of Earth's Atmosphere (Forsythe and Christison, *General Electric Review*).

lengths in the ultraviolet requires expensive equipment and skill, and comparatively few have made such measurements. In the region around 3000A, the data are of somewhat lower accuracy than in the visible region. There are irregularities when the data of Fabry and Buisson and of Abbot are combined in one curve for the transmission of the atmosphere. (Figure 96.) For this reason more direct determinations are desirable.

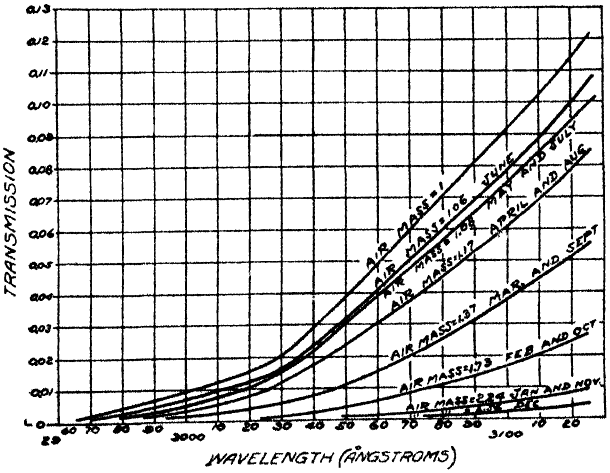

FIGURE 97. Transmission of Atmosphere for Erythema Radiation at Noon, Latitude of Schenectady, N. Y. (Gordon and Benford, *General Electric Review*).

Gordon and Benford[41] give calculated curves (Figure 97) for the atmospheric transmission of radiations of wave-lengths 2900 to 3130A for the "air masses" corresponding to various times of the year. The data of Fabry and Buisson for air mass of 1 were employed, and the transmissions were calculated for the latitude of Schenectady. It is evident that the transmission of the biologically effective rays becomes almost negligible in December as compared with the values of June. These values are also based upon the assumption of cloudless skies, so that the actual values are much smaller in winter months when dark days prevail. These values neglect radiation reflected by clouds and scattered by the blue sky, and radiation received from the sky, which has been estimated to be from one quarter to three-quarters of the amount of direct radiation received from the sun. Regarding this, however, definite statements can scarcely be made. Coblentz,[42] by using a thermocouple and diaphragms subtending an angle of 45 degrees of the sky, found in winter at Washington (low humidity) less than 7 per cent of ultraviolet sky radiation in the total directly incident ultraviolet measured. On a hazy day with high humidity, the ultraviolet sky radiation was 10 per cent of the total incident ultraviolet radiation from the sun. Pettit[43] studied the effect of

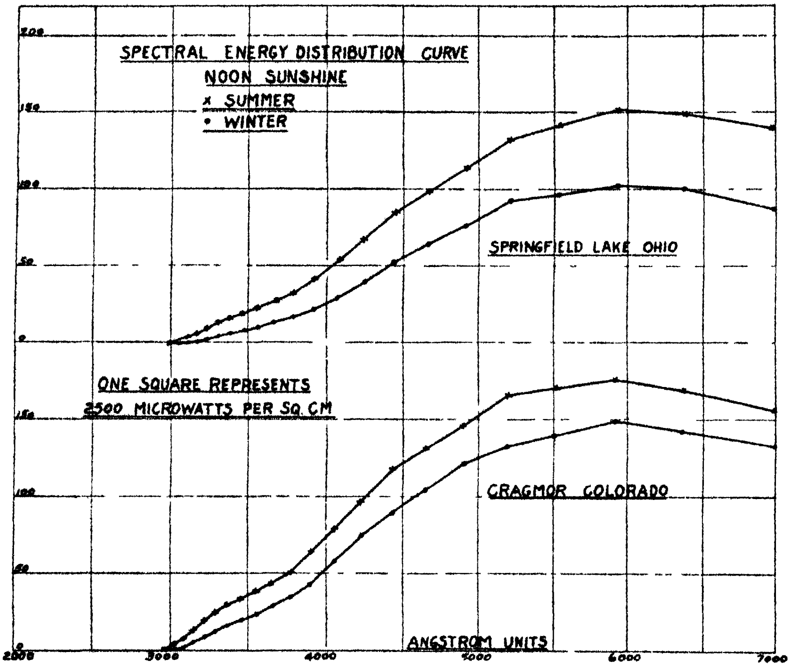

FIGURE 98. Energy Distribution Curve, Sunlight at Cragmor and Springfield Lake. (Greider and Downes, *Transactions Illuminating Engineering Society*).

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[41] Gordon, N T, and Benford, F., *Gen. Elec. Rev*, 33, 283 (1930). For a recent theoretical treatment of data from the Smithsonian observatory at Montezuma, see Kiu, T, *J. phys. radium*, 9, 297 (1938).

[42] Coblentz, W. W., *Trans. Illum. Eng. Soc.*, 26, 576 (1931).

[43] Pettit, E., *Trans. Nat. Tuberculosis Assn. 24th Ann. Meeting*, 110 (1928), cited by Coblentz, W. W.

Table 18.—Transmission of Ultraviolet Rays.

Noon sunshine intensities (watts × 10^{-7} per sq. mm.)

	Antirachitic ultraviolet 2900-3100A	Non-penetrating ultraviolet and visible 3100-6500A	Penetrating red and near infrared 6500-14,000A	Non-penetrating infrared 14,000-120,000A
Springfield Lake,				
October, 1928	1.2	2894	3660	1760
May-June, 1929	2.3	3404	3786	1834
December, 1929	0.49	2440	3720	1615
Cragmoor,				
November, 1928	1.6	3534	4432	1860
June, 1929	5.3	4233	4686	2211
January, 1930	1.1	3390	4565	1915
"Clinical sunlight"*	1.4	3214	4045	1810

* This is the preferred heliotherapy dosage in these institutions corresponding to early morning and late afternoon in summer and noon in winter.

atmospheric scattering. He found on a clear day at Pasadena that the intensity of the ultraviolet radiation from the sky was 11 units as compared with 22 units from the sun plus the sky or 50 per cent of the total. But at Mt. Wilson, the sky contributed only 30 per cent of the total (7 units out of 23.3).

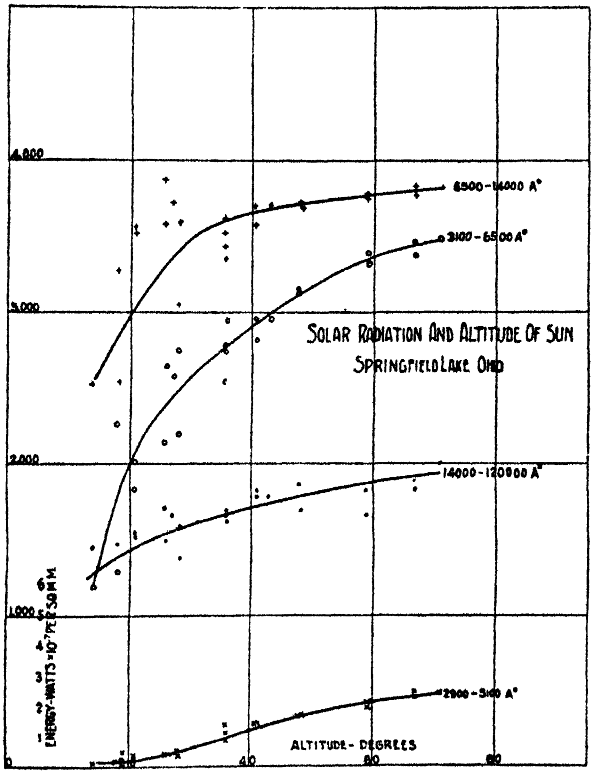

FIGURE 99. Solar Radiation and Altitude of the Sun, Springfield Lake, Ohio. (Greider and Downes, *Transactions Illuminating Engineering Society*).

It is well known that the north sky is richer in ultraviolet than is direct sunlight, but[44] the intensity of light falling in winter at noon on a north window is only about 300 foot-candles as compared with 1100 on a south window.

Greider and Downes[45] reported direct energy measurements at Springfield Lake Sanatorium in Ohio (representative of low altitude locations in this latitude) and at Cragmoor Sanitorium in Colorado ("mountain sun"). Figure 98 shows the noonday values for winter and summer at these locations. The data are summarized in Table 18. Here it is apparent that the variation between summer and winter is less than one to five in the region 2900 to 3100A, which is far less than might be expected from the calculated curves of Gordon and Benford.

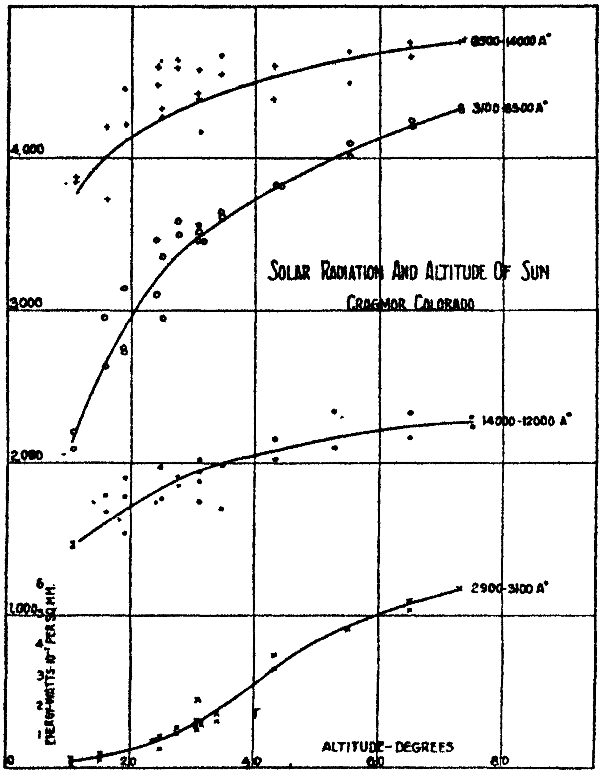

FIGURE 100. Solar Radiation and Altitude of Sun, Cragmor, Colorado. (Greider and Downes, *Transactions Illuminating Engineering Society*).

Greider and Downes have also plotted (Figures 99 and 100), for the two locations, curves of the intensities within the wave-length regions of the table as affected by the altitude of the sun at various hours of the day. These curves can be used to determine the average intensity of the sun at any location at which the transmission of the air is similar to that at either of the locations studied. The altitude of the sun is calculated for the location and time desired and the intensity may then be read from the curves. At the spring and fall equinox the altitude of the sun at noon is 90 degrees minus the latitude. At other times the value is increased or decreased by the amount of the sun's declination. For hours other than noon, the altitude is given by the equation

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[44] Kimball, H. H., and Hand, I. F., *Monthly Weather Rev.*, **50,** 615 (1922), cited by Coblentz, W. W.

[45] Greider, C. E., and Downes, A. C., *Trans. Illum. Eng. Soc.*, **25,** 378 (1930); **26,** 561 (1931).

$$\sin h = \sin \phi \sin \delta + \cos \phi \cos \delta \cos t$$

where h is the altitude of the sun, ϕ its declination, δ the latitude of the place of observation, and t the hour angle, which is approximately 15° for each hour before or after noon.

Such results can of course be only approximations, as they take no account of cloudiness, atmospheric pollution with dust or smoke, or the cleansing effect of rainfall. Coblentz[46] mentions the pronounced effect of dense low-lying strata of finely divided particles from automobile exhausts. The influence of a peak in automobile traffic can be detected in the amount of ultraviolet reaching the earth. Coblentz made photoelectric cell measurements, using a standard screen of barium flint glass. The component of radiation 3130 to 4000A relative to the total ultraviolet 2900 to 4000A measured in June sunlight at sea level was as follows: direct sunlight, 75 per cent; overcast sky during a light rain (the diaphragmed opening in front of the photoelectric cell subtended 18 degrees), 60 per cent; light overcast sky, 50 per cent; blue sky, 55 per cent; dark cloud, 64 per cent; within the laboratory, 4 5 meters from an open window, light from dark clouds through trees, 64-65 per cent. The difference between these values and 100 per cent is a measure of the component 2900 to 3130A.

The Rentschler ultraviolet meter was employed by Meller, Hibben and Warga in a series of observations on the roof of a nine-story building in Pittsburgh. The cathode was mechanically rotated so as to be normal to the sun's rays. A Westinghouse watthour demand meter recorded the results; each line on the chart of the meter, representing the number of impulses in five minutes, is proportional in length to the amount of ultraviolet received at the photo-cell in that period. Records showing the comparative amounts of ultraviolet for an entire day were obtained in this manner. The intermittent obscuring effects of clouds or smoke were readily apparent. Slightly more ultraviolet was recorded on a day having scattered clouds than on a relatively clear day with slightly lower humidity. Even on a clear day there was a 100 per cent change in ultraviolet

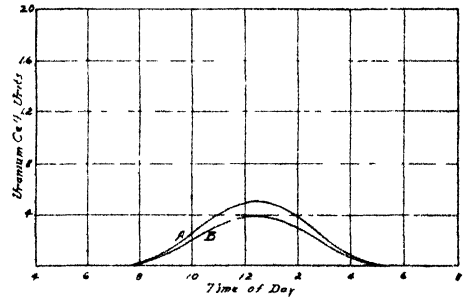

FIGURE 101.

Intensity of Ultraviolet Radiation for December 30, 1930. A. Sun and Sky. B Sky (Kunerth and Miller, *Transactions Illuminating Engineering Society*).

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[46] Coblentz, W. W., *Trans. Illum. Eng. Soc.*, **26**, 572 (1931).

received in a period of 15 or 20 minutes. For comparison, the zinc sulfide and oxalic acid methods were also employed, but exact comparisons could not be made, as the amounts of sky exposure and the sensitivity curves differed in the methods as employed. Meller and Warga [47] studied the effects of air contaminants on the natural light of cities. Similar data were obtained by Kunerth and Miller [48] using the Rentschler meter without the aid of a graphical recorder at Ames, Iowa. Again the units are arbitrary, merely the number of impulses per second. The curves, Figures 101 and 102, show the ultraviolet in the sun and sky light and in the latter alone during the course of days in December and June. The energy from the north half of the sky at noon is approximately equal to one-fifth of the total from sun and sky combined. The variation of sky and sun ultraviolet with altitude of the sun and with month of the year are given in tables. The presence of snow on the ground increases the ultraviolet from sun and sky by about 20 per cent. From the data obtained by the meter exposed to sources otherwise calibrated, it appeared that each impulse of the meter was equal to about 39,000 ergs or 3000 ergs per square centimeter. These authors also presented curves for the visible region from the sun and sky and from the latter alone. The total flux on a horizontal plane throughout the year at latitude 42°N if all days are clear is 16,820,000 lumen-hours per square foot, of which 11,870,000 are received in spring and summer and 4,950,000 in autumn and winter. At noon at the winter solstice, the light from the sky is approximately 16 per cent of the total; at the summer solstice, it is 10 per cent.

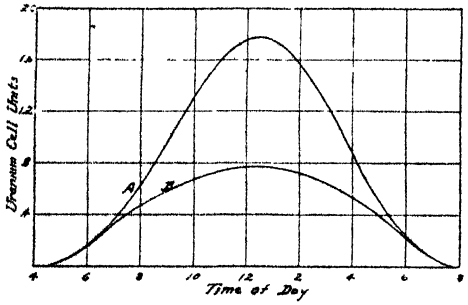

FIGURE 102.

Intensity of Ultraviolet Radiation for June 23, 1931. A. Sun and Sky. B. Sky (Kunerth and Miller, *Transactions Illuminating Engineering Society*).

At New Orleans, the average daily amount of direct solar radiation of wavelengths less than 3130A is less than 0.001 calorie per square centimeter from April to October and between 0.001 and 0.002 during the rest of the year. For the prevention of leg weakness in chickens, the amount required is about 0.00069 calorie per square centimeter daily.[49]

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[47] Meller, H. B., and Warga, M. E., *Am. J. Public Health*, 23, 217 (1933).

[48] Kunerth, W., and Miller, R. D., *Trans. Illum. Eng. Soc.*, 27, 88 (1932).

[49] Mayerson, H. S., and Laurens, H., *Am. J. Physiol.*, 102, 422 (1932).

Part II

Photochemical Processes

Chapter 12

Introduction to the Mechanism of Photochemical Processes

Among the earliest photochemical phenomena observed were the influence of light on the bleaching of linen, and the fading of certain natural dyes and pigments. The effect of light in developing the green color of plants, and the ability of green plants in some way to utilize the energy of the sun in converting carbon dioxide and water to carbohydrates and oxygen were recognized shortly after chemical knowledge had progressed to a stage at which the nature of combustion had become clear. A number of phosphorescent substances early attracted much attention. The photosensitivity of silver salts played an important part in the discovery of the existence of ultraviolet light. (Chapter 1.) The effect of light in accelerating the combination of hydrogen and chlorine, the decomposition of chlorine water, and the reduction of mercuric chloride solutions containing oxalic acid were the subject of a number of early papers.[1]

Grotthuss, in 1817, in studying the fading of alcoholic solutions of ferric chloride and other iron salts, concluded that only light which is absorbed can act chemically. This rather obvious statement, now frequently called the first law of photochemistry, at first attracted little attention, as interest in the energy relations of chemical processes was not yet general. The Grotthuss law was independently rediscovered by Draper in 1843 in the course of investigations on the photochemical combination of hydrogen and chlorine.[2]

The first extensive kinetic studies of a photochemical reaction were those of Bunsen and Roscoe (1855-1862) upon the hydrogen-chlorine combination. (See Chapter 18.) The choice of this reaction was unfortunate, since it is very susceptible to the influence of traces of impurities, the presence of which gives rise to a latent period between the beginning of illumination and the start of the reaction. The observation of an induction period in a reaction so apparently simple led Bunsen and Roscoe and subsequent workers to attach undue importance to induction periods as a feature peculiar to photochemical changes. They did, however, succeed in showing that in general the amount of material transformed in a photochemical change is proportional to the product of the light intensity and the time of illumination. (Bunsen-Roscoe Law.)

Subsequently, a few other reactions were studied, including the oxidation of oxalic acid,[3] the drying of oils, the decomposition of amyl nitrite,[4] the polymerization of anthracene,[5] and of vinyl halides.[6] About 1900 the Italian investigator Ciamician began with Silber a series of researches in which the substances produced by the prolonged action of sunlight upon a wide variety of organic compounds were identified.

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[1] For details of the history of early photochemical work, see Plotnikow, "Allgemeine Photochemie," 2nd ed, 83-105, 1936, de Gruyter, Berlin.

[2] Draper, J., *London, Edinburgh and Dublin Phil. Mag.*, **23**, 401 (1843).

[3] Mohr, F., and Wittstein, G., *Phot. Arch.*, 430, **1864**.

[4] Tyndall, *Jahresb. Chem.*, 108, **1868**.

[5] Fritsche, J., *J. prakt. Chem.*, **101**, 337 (1866); **106**, 274 (1869).

[6] Baumann, E., *Ann. Chem.*, **163**, 317 (1872).

During the first two decades of the present century, the development of the subject of the kinetics of chemical reactions led Bodenstein, Nernst and others to attempt the interpretation of the data on the rates of photochemical reactions in terms of the law of mass action. The difference between the rates of a given reaction occurring in light and in darkness was at first attributed merely to an effect of the light in increasing the velocity constant in the simple mass law expression, no consideration being given to the possibility of a difference in mechanism in the two cases. Attempts were made, although unsuccessfully, by Wildermann[7] to treat the function of the light energy in a fashion analogous to the manner in which Faraday treated electrical energy in the study of electrolysis.

In the case of a few reactions the attempt was made to introduce the intensity of the incident light I_0 in the expressions formulated for the reaction kinetics,[8] as for example, rate $= k' I_0 [A]^m [B]^n$. Van't Hoff in 1904 introduced the assumption that the amount of substance transformed in a reaction is proportional to the amount of the light energy absorbed, rather than merely to the incident intensity, and thereby gave quantitative significance to the Grotthuss-Draper law. Attempts to determine whether or not all of the absorbed energy is effective photochemically were made, notably by Luther and Weigert[9] for the anthracene-dianthracene equilibrium, by Goldberg[10] for the photo-oxidation of quinine by chromic acid, and by Lasareff for the bleaching of dyes.[11]

During this period there were also a number of theoretical studies of photochemical reactions, some dealing with mechanism and others with thermodynamic considerations.[12] Real progress had, however, to await the contributions of the physicist. In the first place, on the practical side, the development of the quartz mercury-vapor arc (Chapter 6) greatly stimulated the study of reactions following the absorption of ultraviolet rays, studies of the wave-length dependence of the yield soon appearing in great number. On the theoretical side, the development of the quantum theory (Chapters 1 and 2) for the first time permitted a beginning to be made in the approach to a satisfactory comprehension of the mechanism by which radiant energy may be absorbed by molecules. Before considering these mechanisms (Chapter 13) it is necessary to discuss the general physical laws of absorption.

The loss in radiant energy of a beam of light which occurs during its passage through a cell containing a liquid or a gas is ascribed to three processes; (a), reflection at the surfaces, (b) scattering by any dust particles in the gas or by colloidal particles in the liquid and (c) absorption by the molecules of the gas or liquid. The last of these is the only one of importance photochemically. In homogeneous pure liquids, scattering may usually be neglected.

Lambert showed that the absorption of approximately monochromatic light varies exponentially with the thickness of the absorbing layer, or $I_x = I_0 e^{-\beta x}$ in which I_0 and I_x denote the incident and transmitted light intensities, x is the thickness of the absorbing layer and β is a number characteristic of the absorbing substance and called its absorption coefficient. Its value varies with the wave-length in a manner characteristic of the substance.

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[7] Wildermann, M., *Z. physik. Chem.*, **42**, 257 (1902); Smits, A., and Aten, A., *Z. Elektrochem.*, **16**, 264 (1910); *Chem. Abs.*, **4**, 1842 (1910).

[8] Bunsen and Roscoe in the hydrogen chlorine reaction and Gros, O., *Z. physik. Chem.*, **37**, 157 (1901).

[9] Luther, R., and Weigert, F., *Z. physik. Chem.*, **53**, 385 (1905).

[10] Goldberg, E., *Z. wiss. Phot.*, **4**, 61 (1906).

[11] Lasareff, P., *Ann. Phys.*, **24**, 661 (1907); **37**, 812 (1912).

[12] Tian, A., *Compt. rend.*, **156**, 1601 (1913); Henri, V., *Soc. Franc. d. Phys.*, **12**, 2 (1911); Berthelot, D., and Gaudechon, H., *Compt. rend.*, **154**, 1597 (1912); **156**, 889 (1913); **160**, 519 (1915).

In 1852, Beer found that in the case of solutions, β is proportional to the concentration, c, of the absorbing component. β may therefore be replaced by αc, α being the absorption coefficient of the absorbing component of the solution. (In cases in which the solute is modified by or reacts with the solvent, Beer's law does not hold.) About this time, Stokes made extensive studies of the phenomenon of fluorescence, which consists in the emission of light of certain wave-lengths by a substance during the time in which it is being irradiated by light of (usually) other wave-lengths. He found that the wave-lengths of the emitted rays are greater than those of the exciting rays. (Stokes's Law.)

THE EINSTEIN PHOTOCHEMICAL EQUIVALENCE LAW

Of the utmost importance to the subsequent development of photochemistry was the derivation by Einstein[13] of the photoequivalent law which states that each absorbed quantum should cause one light-absorbing molecule to react. The derivation of this law, obtained from Planck's radiation law by thermodynamic reasoning, lies beyond the scope of this book. It implies that the number of molecules which have absorbed monochromatic radiant energy may be obtained by dividing the total absorbed energy in ergs (measured physically) by the energy $h\nu$ of a single quantum of light of the frequency employed. To facilitate the evaluation of the quanta of various frequencies commonly employed in photochemistry, Bodenstein and Wagner[14] proposed to employ the term einstein for the energy of N (the Avogadro number, 6.06×10^{23}) light quanta, this being the energy absorbed when each molecule of a gram-molecular weight of a substance absorbs a quantum of radiant energy. They suggested that the intensity of absorbed light be expressed in einsteins absorbed per liter per second.

The idea that the rate of a photochemical reaction may be determined by the number of light quanta absorbed per second had been expressed by Stark as early as 1908[15] preceding the derivation of the photochemical equivalent law by Einstein. Stark believed the primary effect of the light absorbed to be a loosening of the valence electrons, rendering the molecule chemically active. He also distinguished between the primary process of the absorption of light by a molecule and the subsequent secondary processes initiated by the light-changed molecule.

The value of the einstein is commonly expressed in kilocalories for photochemical work. It may be calculated by multiplying the frequency by Planck's constant h (6.54×10^{-27} erg-seconds) and by N (6.06×10^{23}) and dividing the result by 4.182×10^{10} to convert ergs into kilocalories. If the wave-length in Ångström units is first converted into the wave-number by the aid of the graph at the right of Figure 103 it may easily be converted into kilocalories by multiplication by the factor 0.00285. Even this calculation may be avoided by the use of the curve (A *vs.* kcal.) in the same figure.

An appreciation of the magnitude of the einstein at various wave-lengths is of value in enabling one to predict the possibility of effecting a reaction of known activation energy by the use of a given wave-length known to be absorbed by the reacting system.

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[13] Einstein, A., *Ann. Physik*, **37**, 832 (1912); **38**, 881 (1913).

[14] Bodenstein, M., and Wagner, C., *Z physik. Chem.*, **3B**, 456 (1929).

[15] Stark, J., *Physik. Z.*, **9**, 898 (1908).

It is convenient to remember that 10,000A, where the wave-number is also 10,000, corresponds to 28.47 kcal. Then at 5000A the wave-number will be twice as great since it is the reciprocal of the wave-length which is half of 10,000A; the heat value will, therefore, be twice 28.47 or 56.94 kcal. The wave-length, 4000A corresponds to 71 kcal., 3000A to 94.6 kcal. and 2000A to 142.1 kcal. In the x-ray region the values become enormous, but in the far infrared they decrease to such small values as 0.285 kcal. at 100μ.

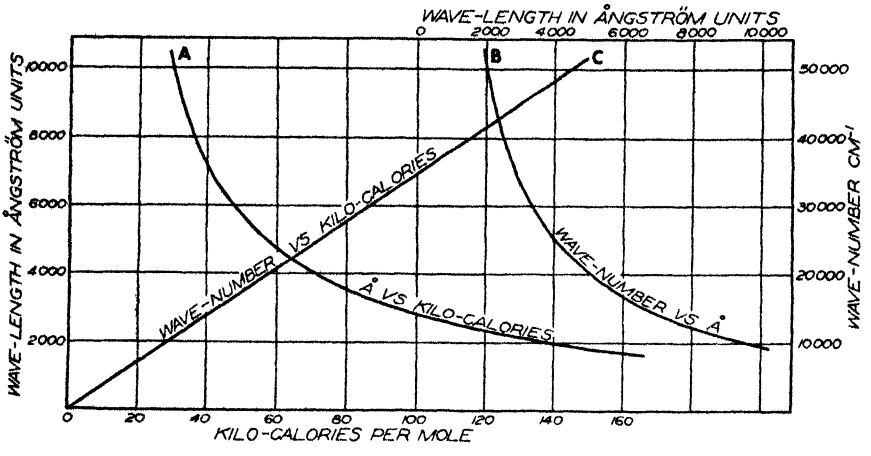

FIGURE 103. Graphs for Conversion of Wave-lengths and Wave-numbers into Kilocalories per Mole and for Conversion of Ångstrom Units into Wave-numbers.

Most photochemical reactions follow upon a process of absorption in which the configuration of the valence electrons has been in some manner altered, and it will be shown in Chapter 13 that visible or ultraviolet radiation is usually required to produce such an electron shift. In the infrared region, the absorbed energy is usually insufficient to produce such effects and instead serves only to alter the rotational motion of the molecule as a whole or the vibrational motion of its component atomic nuclei with respect to each other.[16] There is no fundamental distinction between the reactions due to visible or ultraviolet light and it is not feasible to discuss their effects separately. In order adequately to discuss the effects produced by ultraviolet light it will frequently be necessary to disregard the limitation set by the title of this book and to discuss many reactions due to the absorption of visible light.

Little is known of reactions which may be induced in the regions between the Schumann and the usual x-ray regions. Palmer[17] has noted that radiations from a hydrogen discharge tube passing through a fluorite window into air cause the formation on the outside of the window of a film with metallic luster (soluble in alcohol) which probably is calcium oxyfluoride, and upon the latter a white powder insoluble in water and soluble in dilute hydrochloric acid. Both deposits impede the passage of rays of wave-lengths between 1250 and 1500A.

Reactions Produced by X-Rays. These reactions have received far less study than those produced in the visible and ultraviolet regions. The direct photochemical absorption of the radiation plays a role subordinate to the effects of photoelectrons. The enormous energies of the x-rays make it possible for one quantum on ionizing a molecule to endow the resulting photoelectron with great amounts of kinetic energy.[18] Subsequent effects bear some resemblance to the reactions produced by the bombardment of a substrate with a stream of high-velocity electrons.[19]

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[16] Mecke, R., *Trans. Faraday Soc.*, **27**, 359 (1931).

[17] Palmer, F., Jr., *J. Chem. Physics*, **2**, 296 (1934).

According to Risse,[20] and Fricke and Brownscombe[21] pure, oxygen-free water is not decomposed by x-rays. Comparatively few inorganic reactions have been studied. Noteworthy among these are the hydrogen-chlorine combination,[22] the decomposition of hydrogen peroxide and of potassium persulfate,[23] and certain changes induced in ferrous sulfate,[24] chromic acid,[25] iodine[26] and on photographic plates.[27] Among organic compounds, chloroform and iodoform have been the most extensively studied; hydrogen halides are liberated along with other less investigated products.[28]

General reviews of the chemical effects of x-rays, which in the main are much less extensive than those produced by ultraviolet rays, have been given by Glocker,[29] Günther,[30] Clark and Pickett,[31] and by Fricke.[32] Fricke states that a pecularity of x-ray action is that it frequently involves the production of molecules with unusually high energy states, such as water molecules with at least 91 kcal. per gram molecule.

The Infrared Region. With the possible exception of certain explosions, which may be influenced by infrared radiations,[33] no established case of a chemical reaction brought about by these radiations could be cited by Daniels in 1928.[34] Many attempts were, however, made to find such reactions because of the stimulus of the radiation theory of the origin of the activation energy for chemical reactions, now nearly universally abandoned. This theory which was first suggested by Trautz,[35] and elaborated by Lewis,[36] Perrin,[37] and others,[38] held that the necessary activation energy calculated from the temperature coefficient by the Arrhenius equation, is obtained by absorption by the

[18] Dauvillier, A., *Compt. rend.*, **171**, 627 (1920).

[19] For a further discussion of this topic, see Simons, L., *Brit. J Radiology* (*Roentgen Soc.*, Sect. 23), 124 (1927), or the article of Faila, G., in Duggar, "The Biological Effects of Radiations." New York, McGraw-Hill, **1936**.

[20] Risse, O., *Z. physik. Chem.*, **140**, 133 (1929).

[21] Fricke, H., and Brownscombe, E. R, *Strahlentherapie*, **26**, 319 (1929); **24**, 749, 757 (1927); Fricke, H., and Washburn, M., *Phys. Rev.*, **40**, 1033 (1932); Fricke, H., and Brownscombe, E. R., *Ibid.*, **44**, 240 (1933); Fricke, H., *J. Chem. Phys.*, **2**, 349 (1934).

[22] Leblanc, M., and Volmer, M., *Z. Elektrochem.*, **20**, 494 (1914), Götzky, S., and Günther, P., *Z. physik. Chem.*, **26B**, 373 (1934).

[23] Glockler, R., and Risse, O., *Z. Physik*, **48**, 845 (1928).

[24] Shishacow, W., *Phil. Mag.*, **14**, 198 (1932); Fricke, H., *loc. cit.*

[25] Fricke, H., and Washburn, M., *loc. cit.*

[26] Bordier, H., *Compt. rend.*, **163**, 291 (1916).

[27] Eggert, J., and Noddack, W., *Ber. deutsche physik. Ges.*, 23 (**1924**); Günther, P., and Tittel, H , *Z. Elektrochem.*, **39**, 647 (1933); de Moncetz, A. *Compt. rend.*, **184**, 284 (1927); Villard, P., *Compt. rend*, **184**, 131, 309, 352 (1927); **186**, **1669** (1928).

[28] Glocker, R., *Z. tech. Physik.*, **7**, 571 (1926); *Z. Physik*, **43**, **827** (1927); **46**, 764 (1928), Gunther, P., *Angew. Chem.*, **46**, 627 (1933); Hill, D., *J. Am. Chem. Soc.*, **54**, 32 (1932).

[29] Glocker, R., *Z. tech. Physik*, **9**, 201 (1928).

[30] Günther, P., *Angew. Chem.*, **41**, 1357 (1928); *Ergebnisse tech. Röntgenkunde*, **4**, 100 (1934).

[31] Clark, G. L., and Pickett, L. W., *J. Am. Chem. Soc.*, **52**, 465 (1930); Clark, G. L , and Coe, W. S., *J. Chem. Phys.*, **5**, 97 (1937).

[32] Fricke, H., *Cold Spring Harbor Symposia Quant. Biol* , **3**, 55 (1935).

[33] David, W. T., *Proc. Roy. Soc.*, **108A**, 617 (1925).

[34] **Daniels, F.,** *Chem. Rev.*, **5, 56 (1928).**

[35] **Trautz, M.,** *Z. wiss. Phot.*, **4**, 160 (1906); *Z. anorg. Chem.*, **102**, 81 (1917).

[36] **Lewis, W. C. M.,** *J. Chem. Soc.*, **113**, 471 (1918); *Phil. Mag.*, **39**, 26 (1920).

[37] Perrin, J., *Ann. Phys.*, **11**, 5 (1919), *Trans. Faraday Soc.*, **17**, 546 (1922); *Compt. rend.*, **187**, 913 (1928).

[38] **Baly, E. C. C.,** *Phil. Mag.*, **40**, 1, 15 (1920); *Rec. trav. chim.*, **41**, 516 (1922).

0.032 to 0.104 for the third, extremely high for the fourth, from 0.28 to 1.7 (dependent upon the presence of other gases) for the fifth, 0.024 to 0.25 for the sixth, and 0.25 for the last.

It is important to note the manner in which experiments made with three separate wave-lengths of approximately monochromatic light in the hydrogen iodide decomposition and with two wave-lengths in the case of that of hydrogen bromide afforded a strong confirmation of the theory. Since the magnitude of the quantum increases as the wave-length decreases, it is evident that for the same total amount of energy absorbed at different wave-lengths, the number of quanta absorbed decreases as the wave-length decreases. Therefore, the yield of a given process should be less when the same total energy is employed at a shorter than at a longer wave-length. In the hydrogen iodide decomposition, Warburg found that the ratio of moles decomposed to the calories absorbed (multiplied by 10^5) decreased from 2.08 at 2820A to 1.85 at 2530A and 1.447 at 2070A. The expected values calculated upon the basis of the Einstein law were 1.003, 0.89 and 0.73, respectively. These were in each case very close to half of the observed values. Therefore, in each case, the quantum yield was two. The results in the hydrogen bromide decomposition were very similar.

Warburg was also able to suggest a reasonable explanation of the quantum yield of two by assuming the primary process of absorption by the hydrogen iodide or bromide to consist in a dissociation of these molecules into atoms. A relatively simple sequence of secondary reactions, supported on thermodynamic grounds by Nernst, accounted for the observed quantum yield of two. In this way, granting the correctness of the assumed mechanism of the primary process, the observed quantum yield, despite the fact that it was not unity, could be regarded as a confirmation of the theory. The opinion gradually gained ground that when all factors were taken into account, it would be possible to devise mechanisms for the primary processes and secondary reactions for those photochemical reactions in which extreme values of the quantum yields at first sight appeared less favorable to the theory.

In summarizing his work, Warburg stated[58] that the law has been proved to apply when the quantum absorbed is greater than the energy of dissociation, although in certain cases collisions of the products of dissociation with molecules of foreign gases may lead to a dissipation of their energy so that the law is apparently not followed. He also recognized at this time that in the case of reactions effected by the absorption of quanta smaller than the heat of dissociation, the mechanism of the primary process may involve the formation of excited rather than dissociated molecules. (This type of mechanism will be considered in more detail subsequently.) In this case, under certain conditions, complicating processes may lead to a dissipation of a portion of the energy of some excited molecules so that the quantum yield may be reduced.

Perhaps the present position with regard to the Einstein law has been most clearly stated by Taylor[59] who avoids the idea of equivalence implied by earlier statements of the law by giving it in the form of this Second Law of Photochemistry:

"The absorption of light is a quantum process involving one quantum per absorbing molecule or atom. The photochemical yield is determined by the thermal reactions of the system produced by the light absorption." Henri and

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[58] Warburg, E., *Naturwiss.*, 47, 1058 (1924).

[59] Taylor, H. S., *J. Phys. Chem.*, 32, 516 (1928).

Wurmser[60] recognized the importance of the nature of the primary process in determining the mechanism of a photochemical reaction and discussed the manner (see Chapter 14) in which fluorescence and absorption spectrum studies may be employed in determining the nature of the primary process.

Despite general acceptance of the Einstein law, the possibility has been suggested that in certain cases one quantum of incident energy may activate more than one molecule of the absorbing substance. Basu[61] suggested, possibly as an outcome of Raman spectrum interpretations (Chapter 13), that the incident quantum uses part of its energy in activating the molecule it strikes, and that the remainder is scattered and may activate another molecule.

Investigations of quantum yields have been and are still being carried out extensively because they provide data for testing proposed mechanisms for the reactions studied. Quantum yields are determined for various incident wavelengths of radiation for each new photochemical reaction investigated. The influence upon the yields of many factors, including temperature, variations in the intensity of light, the effects of changes in pressure in gaseous reactions and of concentration in solutions, the effects of different solvents, catalysts and inhibitors, are being actively studied. The more detailed discussion of these topics is given in connection with the individual reactions considered in subsequent chapters.

CHAIN REACTIONS

Allusion has been made to the fact that in certain reactions high quantum yields have been observed. Thus in the hydrogen-chlorine combination, it was stated that the quantum yield was of the order of a million. To explain this, Nernst[62] proposed on thermodynamic grounds the possibility of the following cycle of reactions:

$$\begin{aligned} Cl_2 + h\nu &\longrightarrow Cl + Cl \\ Cl + H_2 &\longrightarrow HCl + H \\ H + Cl_2 &\longrightarrow HCl + Cl, \text{ etc.} \end{aligned}$$

The last two of these reactions evolve heat and can occur spontaneously and be repeated until the hydrogen and chlorine are consumed. Other reactions are conceivable, but are limited in extent. If two chlorine atoms could combine to form a chlorine molecule, they might be expected to dissociate again on absorption of another quantum of radiation. There is, however, an even more cogent reason why neither this process nor the combination of two hydrogen atoms to form molecules can occur to any considerable extent. The combination of two chlorine atoms is exothermic to the extent of 58.5 kcals. For the production of a stable molecule by a collision of two atoms it would be necessary for the energy of recombination to be removed in some manner or the atoms would move apart again. If, however, two atoms of chlorine (or of hydrogen) should chance to collide at the same time with a molecule of an inert gas or with the wall of the reaction vessel, the excess of energy might be imparted to the inert gas molecule or to the wall so that a stable molecule of chlorine (or of hydrogen) might be produced. The inability of atoms to combine to form molecules by two-body collisions thus provides one of the reasons which make it possible for the reactions written above to be so often repeated and thereby make the quantum yield so enormous. In the language of physical chemistry, the chains are said to be long.

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[60] Henri, V., and Wurmser, R., *J. phys. Radium*, 8, 289 (1927).
[61] Basu, K. P., *J. Phys. Chem.*, 33, 1200 (1929).
[62] Nernst, W., *Sitzb. Berlin Akad. Wiss*, 65 (1911).

Although Nernst set up the reaction chain just discussed, he did not at that time suggest all of the details; many others have contributed to the building up of our present concept of chain reactions. Nernst calculated that a similar cycle would be impossible in the case of the combination of hydrogen and bromine, because the reaction $Br + H_2 \rightarrow HBr + H$ is endothermic. Actually, a mixture of hydrogen and bromine is not light sensitive at ordinary temperatures, although a chain reaction occurs at higher temperatures. A further discussion of the more detailed reasoning in regard to these reactions and also the hydrogen iodide decomposition will be given in the chapter on reactions in the gas phase. (Chapter 17.)

Many chain reactions are subject to inhibition by certain substances, which when present in traces, break the chains and lower the yields. A general discussion of the methods of determining the mechanisms of chain reactions has been given by Noyes.[63]

In interpreting the kinetics of chain reactions, three processes require consideration, (a) the chain starting process, (b) the chain terminating process and (c) the chain continuing process.[64]

The Nature of the Primary Process. During recent years an increasing amount of attention has been devoted to an exact determination of the nature of the primary processes of light absorption and the molecular changes affected thereby. Although the book by Kistiakowsky on Photochemical Processes (1928) was predominantly concerned with the kinetics of a number of complete reactions, an indication of the recent shift in emphasis is to be found in the fact that the "Foundations of Photochemistry" by Bonhoeffer and Harteck (1933) devotes 182 pages to the primary process, 39 to secondary reactions and only 59 to the kinetics of overall reactions. At present, efforts are being made to increase our knowledge of the secondary reactions.

Besides the Warburg theory of dissociation as the primary process, others have been proposed. Recent studies indicate, however, that the production of atoms or free radicals either by direct dissociation following the absorption of a quantum or by predissociation (a process described in Chapter 14) is the most commonly encountered primary process.

The early views were rather indefinite. Stark[65] thought the primary effect to be a loosening of valence electrons, rendering the molecules chemically active ("intramolecular photoelectric effect"). Baly and Rice[66] considered ordinary molecules as condensed systems which are non-reactive until opened up, and discussed the relation of absorption bands and fluorescence phenomena to this loosening process. An important paper historically was one in which Stern and Volmer,[67] on the basis of the then current interpretation of band spectra, took issue with the dissociation mechanism proposed by Warburg for the reactions of the hydrogen halides. These authors, influenced by the Bohr theory of the excitation of atoms, explained the primary process of light absorption by molecules in terms of an analogous elevation of the energy level of the molecule by the energy of the absorbed quantum. In this way they made somewhat more precise what is implied in the activation of molecules, a term which had been used earlier by Luther. They discussed particularly the possible ways in which excited molecules might dispose of their energy of excitation. In the first place the energy might be lost by re-emission (fluorescence). A second possibility is the loss of the energy of excitation by inelastic collisions with other molecules, involving conversion of energy of excitation into heat energy. The third and most important possibility is that the excited molecules on colliding with other molecules might utilize this excess energy as energy of activation in bringing about chemical reactions. Thus an activated hydrogen iodide molecule (denoted by *) on colliding with a normal molecule might cause a reaction in which a molecule of hydrogen and one of iodine are produced.

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[63] Noyes, W. A., Jr., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 32 (1935), see also Semenov, N., *Acta Physicochim. U.R.S.S.*, **3**, 245 (1935).

[64] Rollefson, G. K., *J. Phys. Chem.*, **42**, 773 (1938).

[65] Stark, J., "Prinzipien der Atomdynamik," Leipzig, S. Hirzel, II, 207 (1911).

[66] Baly, E. C. C., and Rice, F. O., *J. Chem. Soc.*, **101**, 1475 (1912).

[67] Stern, O., and Volmer, M., *Z. wiss. Phot.*, **19**, 275 (1920).

$$\mathrm{HI} + h\nu \longrightarrow \mathrm{HI}^*$$
$$\mathrm{HI}^* + \mathrm{HI} \longrightarrow \mathrm{H_2} + \mathrm{I_2}$$

In this way it would be possible to explain the quantum yield of two which had been determined experimentally by Warburg.

At the time it was put forward, this view had much to recommend it. Data were being contributed by physicists on the fate of excited atoms and the manner in which the loss of their energy by fluorescence could be quenched or lessened by the presence of inert gas molecules which by collisions could remove the energy. An extension of these considerations to photochemical reactions offered an attractive opportunity for explaining the decreases in quantum yields of gas reactions often observed to occur in the presence of increasing concentrations of foreign non-absorbing gases. Furthermore, at this time relatively little was known of the behavior of atoms or free radicals and their postulation as intermediates by Warburg appeared unnecessarily artificial. Warburg indeed gave as the criterion for the occurrence of dissociation in the primary process the stipulation that the quantum energy of the absorbed radiation must be larger than the heat of dissociation of the molecules, and recognized that the absorption of lesser quanta could lead only to the production of excited molecules. For these reasons, attention during the early 1920's was predominantly devoted to the activated molecule theory of the primary process. Noddack[68] explained the lowering of the yield in the reaction between chlorine and trichlorobromomethane in carbon tetrachloride which accompanies increasing dilution by the solvent on the basis of this theory. The more frequent collisions of the activated molecules with indifferent carbon tetrachloride molecules deactivated them so that the photochemical reaction had less chance of occurring It was also pointed out by many that if an activated molecule did not collide with a molecule with which it might react within its life period (10^{-8}-10^{-9} second)[69] it would lose some of its energy by fluorescence; if, on the other hand, it collided with an indifferent molecule it could lose its energy in the collision. In a gas at normal pressures the loss of energy by fluorescence would not be expected to be important, this effect becoming pronounced only when the time interval between collisions of the excited molecules with the reactant molecules becomes comparable with the mean life of the excited state.

Attempts were made to extend the theory of activated molecules to account for chain reactions, the assumption being made that such an excited molecule enters into reaction with a normal molecule and produces another excited molecule as one of the products in a manner analogous to that in which atoms functioned in the chain theory of Nernst. It need only be said here that such energy chains have been shown to involve certain difficulties and that, in the main, there is rarely any necessity for assuming their occurrence in explaining photochemical processes. Elaborate attempts were also made to picture the change involved in activating molecules in terms of the orbits in which the valence electrons move.[70] Such attempts have been rendered unnecessary by developments of the theory of valence and of molecular energy states.

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[68] Noddack, W., *Z. Elektrochem.*, 27, 359 (1921).

[69] Cf. Mukerji, B. K., and Dhar, N. R., *Z. Elektrochem.*, 31, 283 (1925).

Brief mention may be made at this point of an early theory of Weigert[71] which assumed that at least two molecules of gaseous halogens participate in the absorption process, an electron being believed to be displaced from one to the other. The resulting molecular complex acted as a nucleus at which subsequent reactions proceeded. This theory has not survived, although a vestige remains in the modern treatment of the photochemical processes occurring in alkali-halide crystals.

By 1924, Bowen,[72] in comparing the mechanisms (dissociation versus excited molecule) of the primary process involved in the photochemical reactions by which the hydrogen halides are formed showed that the dissociation theory gives a quantitative explanation of all the experimental facts if due consideration is given to the heats of reaction and if it is assumed that a large evolution of heat favors a spontaneous reaction and that an endothermic secondary reaction does not proceed. He pointed out that a clarification of the then conflicting points of view in regard to the nature of the primary process awaited a physical interpretation of the data of the band absorption spectra of gases. The most marked feature of the development during recent years has been the application of the theory of band spectra to the interpretation of the primary processes of photochemical reactions. For this reason the next chapter digresses to give a brief introduction to the theory of the origin of band spectra, after which it becomes possible in Chapter 14 to discuss the contributions which spectroscopy is able to make to an understanding of the nature of the primary process in photochemical reactions occurring in the gas phase.

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[70] Waldbauer, L., and Patton, I. J., *J. Phys. Chem*, **31**, 1433 (1927).

[71] Weigert, F., *Ann. Physik*, **24**, 243 (1907); *Z. Elektrochem.*, **28**, 456 (1922); Weigert, F., and Kellermann, K., *Z. physik. Chem.*, **107**, 1 (1923); Weigert, F., *Ibid.*, **102**, 416 (1922); **106**, 407 (1923). See, for objections, Kornfeld, G., *Z. physik.*, **108**, 118 (1924).

[72] Bowen, E. J., *J. Chem. Soc.*, **125**, 1233 (1924); *Trans. Faraday Soc.*, **21**, 543 (1925).

Chapter 13

Molecular Spectra and Their Relation to Photochemistry

Early workers on the absorption or emission spectroscopy of molecules used spectroscopes of low resolving power and observed spectra characterized by more or less regularly recurring flutings or bands. These apparently continuous bands gave rise to the term "band spectra," really a misnomer since instruments of higher resolving power have long since revealed the fact that in many cases, the "bands" in the spectra of gaseous molecules are really composed of great numbers of finely spaced lines.

Molecular spectra have been very actively investigated within the last two decades. The literature dealing with them is of vast proportions and is couched in a somewhat unfamiliar notation, unfortunately necessary because of the complexity of the interrelations between the forms of motion characterizing molecular energy states, the transitions between which give rise to the many lines. In the study of the emission spectra of molecules much effort has been required merely to identify the molecule or molecular fragment giving rise to a given spectrum or arrangement of lines and bands under the experimental conditions of excitation. In many instances it has been demonstrated that the spectrum must be attributed to the presence of molecules of a type unfamiliar to a chemist (BO, He_2, BaH, etc.).

Early investigations were limited to the accurate measurements of the wavelengths of the many lines observed in the emission or absorption spectra of various substances produced under definite experimental conditions. Later phases of the work were concerned with the identification of the molecules responsible for these spectra, and, following this, with the classification of the lines into bands, of the bands into groups of bands, and of these groups into larger series. Next came the representation of these observed facts by mathematical expressions. Only in the past thirty years has it been possible to make physical interpretations of the relationships thus demonstrated.

The study of molecular spectra has provided the chemist with a tool which has yielded data valuable in fields remote from that of photochemistry. The spectra provide information as to the structures, sizes and shapes of molecules, have led to the discovery of the isotopes of several elements and have furnished values for heats of dissociation, bond strengths, heat contents, entropies, specific heats, free energies, equilibrium constants and heats of activation in many cases more readily and more accurately than are secured by the older methods of thermochemistry.[1] Progress in the application of the methods of wave mechanics to the interpretation of band spectra has been so rapid as to have led Kemble[2] to express the hope that "in a few years we may understand the fundamental principles of molecule formation as definitely as we now understand the principles of dynamo design."

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[1] Giauque, W. F., and Wiebe, R., *J. Am Chem. Soc.*, **50**, 101, 2193 (1928); **52**, 4808, 4816 (1930); **53**, 507 (1931); Godnev, I. N., *Ibid.*, **58**, 180 (1936); Kassel, L. S., *Phys. Rev.* **43**, 364 (1933); *J. Am. Chem. Soc.*, **55**, 1351 (1933); *J. Chem. Physics*, **1**, 576 (1933); Zeise, H., *Z. Elektrochem.*, **39**, 758 (1933); Franck, J., *Ibid.*, **36**, 581 (1930); Bryant, W., *Ind. Eng. Chem*, **25**, 820 (1933); Rodebush, W., *Chem. Rev.*, **9**, 319 (1931); Kassel, L. S. *Chem. Rev.*, **18**, 277 (1936); Witmer, E., *J. Am. Chem. Soc*, **56**, 2229 (1934).

[2] Kemble, E. C., *J. Frank. Inst.*, **206**, 27 (1928).

The complexities of spectra and the extensive mathematical equipment required for their interpretation make this a field for specialists. Fortunately, a detailed knowledge of this field is not essential to an understanding of much of the work in photochemistry. The discussion in this chapter is intended only to furnish the chemist not versed in spectroscopy with enough of the present viewpoint regarding molecular spectra to permit him to comprehend the manner in which the character of the spectrum within a given wave-length region shows whether the absorption has produced excited molecules or has led to a dissociation of the molecule into atoms or free radicals. The character of the molecular spectrum thus gives a clue to the nature of the primary process of absorption. For the most part, only the spectra of diatomic molecules will be considered, since these have been more completely interpreted than have the vastly more complicated spectra of polyatomic molecules.

Representative of the band spectra of diatomic molecules is that of phosphorus nitride, a portion of which is reproduced in Figure 104. Each of the dark regions which fades out gradually from a sharp edge is known as a band. Some molecules produce spectra in which the fading from the edge of the bands to more and more widely separated and weaker lines extends toward the shorter wave-lengths. In the spectra of others the opposite is true. The bands are accordingly said to be degraded toward the violet or toward the red.

The edges of the bands recur in a somewhat regular sequence and so form a band group. Furthermore, over wider spectral ranges, the various groups of bands may also follow in sequence to form a system of bands. The complete emission spectrum of a substance may under certain circumstances consist of several band systems. Cyanogen, for example, has one system between 4000 and 5000A and another in the red. Different portions of the complete spectrum may be revealed by the use of different methods of excitation. The complete spectrum of a diatomic molecule composed of unlike atoms may extend from the far infrared to far in the ultraviolet.

Deslandres,[3] a pioneer in the empirical study of molecular spectra, demonstrated relations between the wave-numbers of the lines of a band and also between those of the heads of the bands of a group. As in the case of atomic spectra, progress in the interpretation of such relationships came only with the application of the quantum theory. The wave-numbers of the individual lines depend upon the differences between energy states of the molecule. In discussing the possible energy levels of a molecule there must be considered certain molecular and intramolecular motions which were not encountered in the discussion of the energy levels of atoms. The molecule may rotate as a whole about its center of gravity and the two atomic nuclei may vibrate with respect to each other along the line joining their centers. Each of these types of motion is quantized, only discrete rotational and vibrational energy levels being possible. In addition, as in atomic spectra, transitions between electronic energy levels must be considered.

Even before the advent of the Bohr theory of the quantization of the electronic states of atoms, Bjerrum[4] suggested that transitions between various rotational

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[3] Deslandres, H., *Compt. rend.*, **103**, 375 (1886); **104**, 972 (1888); **134**, 747 (1902); **138**, 317 (1904); *Ann. Chim. Phys.*, **15**, 5 (1888); *J. de phys.*, **10**, 276 (1891).

[4] Bjerrum, N., *Nernst Festchrift*, 90 (1912); cited in Baly, E. C. C., "Spectroscopy," Vol. 3, London, Longmans Green, 1927.

FIGURE 104. Band Spectrum of a PN Molecule (From Herzberg, "Atomic Spectra and Atomic Structure," New York, Prentice-Hall, 1937).

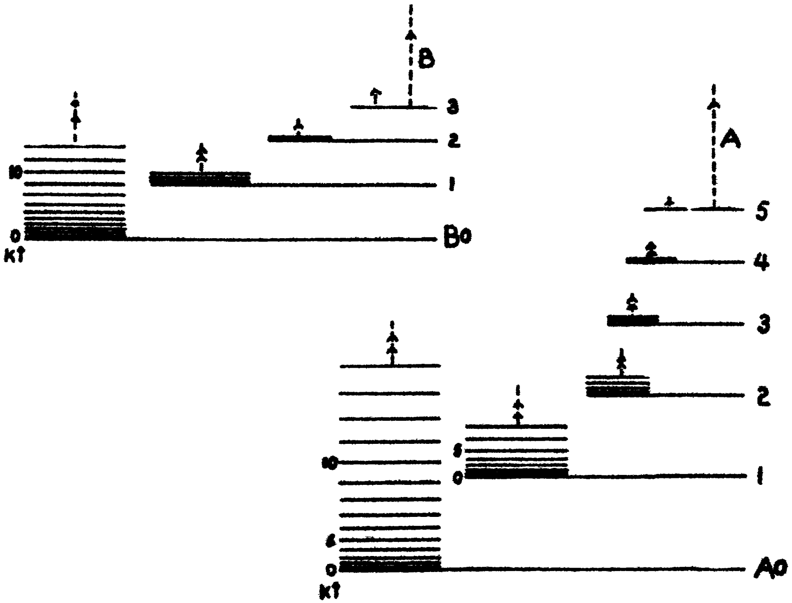

FIGURE 105. Schematic Energy Level Diagram for Diatomic Molecule (Mulliken, *Chemical Reviews*).

states of the molecule might account for the energy differences corresponding to the lines in the far infrared spectra of diatomic molecules. Schwarzschild[5] employed a series of integral quantum numbers in an expression by which the quantized moment of momentum of the rotating molecule could be used in calculating the wave-numbers of the various lines corresponding to shifts between rotational states. Heurlinger[6] introduced vibrational quantum numbers for dealing in a similar manner with the to-and-fro oscillations of the nuclei with respect to each other. Kratzer[7] developed the theory of the vibrations of an anharmonic oscillator in terms of the approximation that the motions of rotation and vibration do not mutually influence each other. He also employed selection principles analogous to those employed in atomic spectra for the restriction of the transitions which are permitted between various rotational and vibrational states.

In general, then, three forms of energy contribute chiefly to the total energy of each state between which the line-producing transitions occur. The total energy may be represented by $E_{\mathrm{el}} + E_{\mathrm{vib}} + E_{\mathrm{rot}}$. The order in which these have been listed is that of decreasing magnitudes of the energy contributions. In more accurate expressions, the effects of interactions between the various forms of motion must be taken into account. In the energy level diagram of a molecule there is for each electronic state a series of more closely spaced vibrational states designated by successive quantum numbers, and for each vibrational level a series of still more closely spaced rotational levels, also designated by integral quantum numbers. (Figure 105.)

The electronic state of lowest energy is termed the ground state; the other electronic states are excited states, the excitation energies being of the same order of magnitude as those of excited atoms. The successive energy increments between the electronic states vary in different molecules from about 1 to 10 electron-volts, corresponding to 1 to 10 times 23 kcal. The lines produced by transitions between such levels will lie in the visible or ultraviolet regions of the spectrum. Usually the number of electronic levels of a molecule available for transitions to produce lines in the accessible portions of the ultraviolet is much smaller than in the case of atomic spectra. Electronic term series are observed only in exceptional cases. The series limits corresponding to the ionization potentials of molecules are rarely encountered in the spectra most frequently referred to in the following chapters.

The separation of the vibrational levels is usually only 0.1 to 0.01 as great as that between the electronic levels (or about 1000 wave-numbers). The difference between rotational levels is very small, about 0.01 that between the vibrational levels, or from ten to 100 wave-numbers.[7a] Transitions between terms in accordance with certain selection principles give rise to the spectral lines, the wave-numbers of which are readily obtained by subtraction of the values of the energy levels (terms) expressed as wave-numbers. In the most general case in the visible and ultraviolet regions, the lines are due to transitions in which the electronic, vibrational and rotational energies each suffer change. For a given electronic shift, there may be a diversity of simultaneous changes in the vibrational and rotational levels. This accounts for the great number of lines of molecular spectra. Transitions between two electronic levels give rise to a band system and those between other electronic levels to other band systems. Each band in the series comprising a single band system arises from a shift in the vibrational quantum number superposed upon one and the same shift between electron levels. The many fine lines which make up the structure of each band are determined in analogous fashion by the possible rotational shifts which may accompany the electronic and vibrational shifts which locate the position of the band edge.

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[5] Schwarzschild, K., *Preuss. Akad. Wiss., Sitzber.*, 548 (1916).

[6] Heurlinger, T., *Physikal. Z.*, **20**, 188 (1919); *Z. Physik*, **1**, 84 (1920).

[7] Kratzer, A., *Z. Physik*, **3**, 289 (1920).

[7a] In the light molecules, H_2, He_2, LiH, the rotational levels are more widely separated.

Spectra may be encountered in the production of which neither electronic nor vibrational transitions have occurred. Since in these the transitions are exclusively between rotational states, such spectra are called pure rotation spectra. Since the rotational states lie very close together, transitions between them involve the emission or absorption of but very small amounts of energy so that the corresponding rotational lines have very low frequencies and lie far in the infrared. In practice, these lines are observed only in absorption spectra and have been comparatively little studied because of experimental difficulties. During the production of such spectra the molecules are always in the ground electronic state.

The frequencies in the near infrared region correspond to greater energy differences between terms, so that in their production certain transitions between the more widely separated vibrational levels are involved. Each such transition corresponds to a band, and as previously stated, each line within the structure of a given band corresponds to a change in the rotational state as well as that vibrational change which is concerned in the production of every line within that band. These near infrared spectra originating in simultaneous vibrational and rotational transitions are known as rotation-vibration spectra.

In the visible and ultraviolet regions electronic transitions are concerned and are accompanied by simultaneous vibrational transitions each producing a band and by rotational transitions responsible for the lines composing each band. Thus, each line in such a band corresponds to the same electronic shift and to the same vibrational shift, but the vibrational shift is different in the case of each line of each of the other bands The origin of each band may be located by the frequencies corresponding to vibrational transitions between the zero rotational levels of successive vibrational levels, that is, the frequency is $\nu = \nu_{el} + \nu_{vib}$ corresponding to $\nu_{rot} = 0$.

In the production of near infrared absorption spectra, the limited energy in each absorbed quantum usually suffices to excite but a very few vibration levels so that but a few bands (one to three or four) can appear. But the number of bands in the visible or ultraviolet regions accompanying each electron shift may be much greater, the vibrational quantum numbers may reach ten or more, and the spectra are accordingly much more complex. Molecules composed of two like atoms (H_2, N_2, etc.) exhibit no absorption in the infrared from 100μ to 1μ and lack pure rotation and rotation-vibration spectra. This does not mean that such molecules lack rotational or vibrational energy but indicates only that these symmetrical molecules lack the electrical moments whose existence is a prerequisite for interaction with electromagnetic radiations. When an electronic excitation has been brought about in such a symmetrical molecule, the resultant electronic structure is such as to make the molecule an electrical dipole capable of interacting with electromagnetic waves. For this reason the type of information yielded for heteropolar molecules by infrared rotation-vibration spectra can be obtained in the case of homopolar molecules only in the visible or ultraviolet regions. Even then, the spectra of these bands will be due to the transitions between rotational and vibrational states of the electronically excited molecules rather than that of the molecules in the ground electronic state. Information regarding the vibrational and rotational levels of homopolar molecules may, however, be derived from studies of the Raman spectra to which brief reference is made in another section.

In general, the far infrared spectrum yields information about the rotational levels in the ground or electronically unexcited state of heteropolar molecules, and the near infrared region does the same for both the rotational and the vibrational levels. Similar information regarding the vibrational levels of electronically excited molecules is obtained from the series arrangement of the visible and ultraviolet bands; fine structure studies of the individual bands in these regions give information about the rotational term separations. To obtain similar data for the ground state it would be necessary to utilize the experimentally more difficultly accessible infrared spectra, or else to use the newer Raman spectra.

Pure Rotation Bands and the Information They Yield

Spectra resulting from transitions between purely rotational states lie in the far infrared from 50μ to 200μ. Those of diatomic molecules consist of a series of equidistant lines, the separation of which yields valuable information regarding the molecular dimensions.

In a diatomic molecule rotating as a whole about an axis through its center of gravity, one of the three possibilities for rotation has a zero moment of inertia and the other two are equal. There is accordingly only one series of rotational quantized energy states which needs to be considered. The energies of the states are determined by the integral quantum numbers and by the moment of inertia of the molecule. This latter in turn is dependent upon the masses of the atoms composing the molecule and their separation. It is thus evident that, since the masses of the atoms are known, measurement of the energies of the various rotational states should furnish important information in regard to the sizes of the molecules. The manner in which this may be done lies beyond the scope of this book. This topic is mentioned merely to indicate the nature of the information it is possible to derive from band spectra.

The wave-number of a rotational state is given by $\frac{h}{8\pi^2 I} m(m+1)$ in which m may be zero or an integer and I is the moment of inertia. A selection rule states that the quantum number m may change by only one in a transition producing a line. Therefore, the wave-number of a line in this spectrum is given by the difference between two such terms, one having an m value one greater than the other. The expression for a given line reduces to $\nu = \frac{h}{4\pi^2 I} m$. The wave-number separation of a series of such lines corresponding to successive integral values of m thus permits of a calculation of I, the moment of inertia of the molecule. From the moment of inertia and the masses of the atoms, it is then possible to calculate the radius of the separation of the atomic nuclei. In exact work, a slight correction is required for a change in I due to centrifugal force in the higher rotational states.

The Vibration-Rotation Bands

Absorption of a larger near infrared quantum produces a transition between vibrational states and is responsible for the production of a band. The corresponding wave-length, if there were no accompanying rotation, would locate the position of the band and would be called the zero line. Actually the absorption spectra of diatomic molecules fail to show this line since a selection principle requires that there be a rotational shift accompanying each vibrational transition. As previously stated, the series of lines composing the band is caused by a series of simultaneous rotational transitions. The expression for the frequency of each of the lines of a band is given by

$$\nu = \nu_0 + \frac{h}{4\pi^2 I} m$$

in which ν_0 locates the origin of the band and the second term accounts for the effect of the rotational transition. As the rotational quantum number may either increase or decrease by one, the lines corresponding to transitions from each initial rotational state will be located on each side of ν_0. The impression given by the band as a whole is that of two bands each composed of a number of sharp lines, the separation of which is similar to that of the lines of a pure rotation spectrum. The separation of the lines composing a band gives evidence regarding the rotational quanta and, as has been shown in the case of pure rotation spectra, from these much can be learned of the size and shape of the absorbing molecules.

The lines composing a band may be classified into two groups or branches. One series occurring on the long-wave side of the origin has the second term negative in the expression just discussed and is called the negative or P branch. A series in which m is positive occurs on the short-wave side of the origin and is called the positive or R branch. Transitions in which m does not change would give rise to a third branch called the zero or Q branch. Since they would violate the selection principle, the Q branch is usually lacking in the rotation-vibration spectra of the diatomic molecules, but is encountered in the spectra of polyatomic molecules as well as generally in electronic band spectra.

In the earlier attempts to interpret the successive bands in a vibration-rotation spectrum, the diatomic molecule was treated as an harmonic oscillator the vibrational states of which were quantized. The energy in a given state was denoted by $E_v = h\omega(v + \frac{1}{2})$, neglecting the contribution due to rotation. The necessity for the use of $\frac{1}{2}$ was found empirically, but has since been justified on theoretical grounds which cannot be here discussed. ω is the fundamental frequency of vibration of the nuclei and v is a quantum number which may be zero or an integer. When v is zero (the so-called vibrationless state) the molecule still possesses the vibrational energy $+\frac{1}{2}h\omega$. Successive integral values of v then give the successive vibrational states and transitions between these the zero lines of successive bands. To obtain the structure of the band use must be made of the more complete expression containing the rotational contribution to the energy state. From this theory but one infrared band would be expected. Its zero line is given by the fundamental frequency and its structure by the rotational effects. No matter whether the vibrational transition is from $v=0$ to $v=1$ or from $v=3$ to $v=4$, the zero line might be expected to be in the same position. (If the electronic structure of the molecule be altered as in the case of band spectra in the visible and ultraviolet regions, the fundamental frequency is, however, altered.) Actually, however, the diatomic molecule is not a true harmonic oscillator; the binding between the atoms is not elastic since the attractive force between them does not increase to infinity as they are more and more widely separated.

In the harmonic oscillator the restoring force K per cm. displacement z of the atoms from their equilibrium separation is proportional to this displacement.

$$K = -a\,z$$

The true frequency is related to a by the expression

$$\text{Frequency} = \nu c = \frac{1}{2\pi}\sqrt{\frac{a}{\mu}}$$

in which c is the velocity of light, ν the wave-number of the fundamental frequency and μ the "reduced mass" of the molecule, by which is meant the product of the masses of the two atoms divided by their sum. In the case of the non-harmonic oscillator, it is necessary to employ a power series in writing the binding force between the atoms,

$$K = -az + bz^2 + cz^3 \ldots$$

This means that higher powers, at least the second, of the vibrational quantum number must be employed in expressing the vibrational term wave-numbers.

$$\nu = (v + \tfrac{1}{2})\omega_0 - (v + \tfrac{1}{2})^2 x\omega_0.$$

Here x is a factor for the anharmonicity of the binding and determined by the cofficients in the power series written above. The differences between successive terms responsible for the origin of the bands are thus equal to $\omega - 2x\omega(v + 1)$. This makes it evident that several bands corresponding to different values of n may appear in a system. From this relation it appears that the separation of the successive bands of a system tends to decrease as the quantum number attains high values. Actually only a few bands are usually encountered in the near infrared spectra.

In polyatomic molecules,[8] there may be several modes of vibration, including deformation vibrations in non-linear molecules. The resultant band spectra produced as a result of the interplay of these various forms of motion may be quite complex. The near infrared spectrum of ammonia, for example, contains 13 bands. In each series of bands those involving transitions between states of higher quantum numbers decrease rapidly in intensity, so that those capable of yielding accurate measurements are relatively few.

Raman Spectra. Much of the information regarding the vibration frequencies of various linkages can be more readily obtained by observations of their effects upon the scattering of visible and ultraviolet monochromatic radiations: in 1928, Raman[9] observed that the ordinary radiation scattered by molecules in dust-free liquids or gases contains, besides the radiation of the same wave-length as the incident light, still other wave-lengths, usually of lower frequencies, together with some lines of lower intensity but of higher frequencies The wave-numbers corresponding to the shifts of the frequency of the new lines in the scattered radiation from the frequency of the incident radiation are in general related to the frequencies of infrared bands. The importance of this new tool led to a large number of investigations of a wide variety of substances, solids, liquids, gases and solutions. The information secured with Raman spectra on the structure of organic molecules has been reviewed by Dadieu and Kohlrausch.[10]

The discussion of the physical aspects of the Raman effect lies beyond the scope of this work. Its value consists in part in the fact that it permits a determination of frequencies of vibration of molecules in their ground states and in part in that it is also applicable to homopolar molecules.

ELECTRONIC BAND SPECTRA

Electronic excitation is the chief alteration produced in a molecule by the absorption of visible or ultraviolet radiations. The early development of the theory was due to Heurlinger, to Lenz [11] and to Kratzer.[12]

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[8] See Villars, D. S., *Chem. Rev.*, **11**, 369 (1932); Dennison, D. M., *Rev. Modern Physics*, **3**, 280 (1931).

[9] Raman, C. V., and Krishnan, K. S., *Nature*, **121**, 501, 619 (1928); *Indian J. Physics*, **2**, 387 (1928); **6**, 263 (1931); *Trans. Faraday Soc.*, **25**, 781 (1929). The effect was independently discovered by Landsberg and Mandelstam, *Naturwiss.*, **16**, 557 (1928).

[10] Dadieu, A., and Kohlrausch, K. W. F., *Ber.*, **63B**, 251 (1930); translation by Hollaender, A., *J. Opt. Soc. Am.*, **21**, 286 (1931). Hibben, J. H., "The Raman Effect and Its Chemical Applications," Reinhold Publishing Corp., New York, 1939.

All lines accompanying a single given electronic transition belong to the same band system. The various bands within the system are ascribed to the accompanying vibrational transitions and the lines within the bands to the rotational shifts. Although but a few bands of the ground electronic state can be observed in infrared spectra, in the visible and ultraviolet band spectra a larger number of bands corresponding to quantum numbers as high as ten or twenty may be observed. In some cases it is possible to follow the asymptotic convergence of the successive bands toward a limit. This implies the gradual disappearance of the binding force between the atoms on increased separation during vibrations.

The considerations relating the various bands (taken from their zero lines) to each other are similar to those in the case of the infrared vibration-rotation spectra, and similarly, the structure of each band is analogous to that of the infrared band, a Q branch being also usually present. The close packing of the lines near the head of a band often makes it very difficult to disentangle the band structure. During the electronic shift there is a change in the structure of the molecule which involves a change in its moment of inertia.

Each line is given by an expression which involves a term for the contribution due to the electron shift, one for the vibration shift (together with a second power correcting term for the anharmonicity of the oscillator) and a term for the rotational shift together with a second power term introduced because of the change of the moment of inertia during the electronic shift. The structure of the band is thus given by $\nu = \nu_{el+os} + bm \pm cm^2$, in which b is approximately $h/4\pi^2I$, the I referring to the lower electronic state. The constant c (about 0 1b) may be positive or negative and corrects for the change in the moment of inertia. When negative, as m increases, it yields the *R* branch. As cm^2 grows faster than bm, the lines crowd together. At some value of m, cm^2 exceeds bm (the head of the band) so that with larger values of m there results a decreasing series with increasing spacings of the lines. The position of the head of the band depends on the ratio of b to c. When c is negative, the head occurs on the high frequency side of the origin. Negative values of m yield the P branch; these lines will gradually decrease in frequency and have greater separation as m increases. The intensities of the lines decrease and the band shades off on the lower frequency side The Q branch lies between the R and P branches.

The complete interpretation of the band spectrum of a compound is a matter of great difficulty largely because of the great number of energy states which may be possessed by a molecule. Even the classification of the lines into the bands, series of bands, and electronic band systems is rendered very difficult because of overlapping of the various structural units and because the electronic energy states, like those of atomic spectra, exhibit multiplicity. The early development of the theory [13] was based upon a formal analogy between line and band spectra, the electronic terms of each involving various quantum numbers; similar selection principles were used. The systematization of the relations between the electronic structures of diatomic molecules and the nature of their band spectra is due in large part to Mulliken,[14] who proposed a notation for designating the state of each electron and of the molecule as a whole.[15]

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[11] Lenz, W., *Verh. deutsch. Phys. Ges.*, **21**, 632 (1919).

[12] Kratzer, A., *Ann. Phys.*, **67**, 127 (1922); **71**, 72 (1923).

[13] Mecke, R., *Physik. Z.*, **26**, 217 (1925), *Z. Physik*, **28**, 261 (1924); **32**, 823 (1925); **31**, 709 (1925); **36**, 795 (1926); *Naturwiss.*, **13**, 698 (1925). Hund, F., *Z. Physik*, **36**, 657 (1926); **51**, 759 (1928); Birge, R. T., *Nature*, **117**, 300 (1926).

[14] Mulliken, R. S., *Proc. Nat. Acad. Sci.*, **12**, 144, 151 (1926); *Phys. Rev.*, **29**, 391, 921 (1927); **30**, 138, 150, 175, 785 (1927); **32**, 186, 761 (1928); **33**, 730 (1929).

[15] Other important contributions were made by Birge, R. T., *Phys. Rev.*, **27**, 245 (1926); Kemble. E. C., *Z. Physik*, **35**, 286 (1925); *Proc. Nat. Acad. Sci.*, **10**, 274 (1924); *Phys. Rev.*, **25**, 1 (1925); Kratzer, A., *Z. Physik*, **33**, 144 (1925). The subject is one for a specialist.

In analogy with the S, P, D, . . . terms for atoms there are recognized Σ, Π, Δ terms for molecules. These correspond to the successive values of a quantum number Λ (0, 1, 2). While in the atom, the orbital number L gives the resultant orbital angular momentum of all the electrons, in the molecule the presence of the two nuclei introduces certain complications. But, since the internuclear line is still an axis of symmetry, the component of the orbital angular momentum along this line remains a constant, which may be measured in units of $h/2\pi$. As in the case of the atom, the resultant spin angular momentum of all the electrons serves as another quantum number S. Dependent upon its value (0, ½, 1 . . .) there may be singlet, doublet, triplet states of the molecule. The multiplicity is given by $2S+1$ and is denoted in writing a term by an upper left-hand index before the term symbol, which is derived from the value of Λ. The ${}^2\Sigma$ represents a state with $\Lambda=0$, $S=\frac{1}{2}$, a ${}^1\Pi$ term a state with $\Lambda=1$, $S=0$, and a ${}^3\Delta$ term a state with $\Lambda=2$, $S=1$. As with atoms, S is integral or half-integral depending on whether the total number of electrons in the molecule is even or odd. The multiplicity is even for uneven electron numbers and uneven for even electrons. Other features of term designations may be found in specialized treatises.

It is unnecessary to discuss here the various selection principles which have been given to account for the relative frequencies of the transitions between various molecular energy states. Much is known in regard to the lives of the excited states, but the methods by which these may be calculated by means of the Schrödinger equations are primarily of interest to the specialist. For electron transitions in the wave-number range 10^4-10^5 cm.$^{-1}$, the excited states have a life of about 10^{-8} second. For transitions in vibration frequencies in the range of 10^2-10^3 cm.$^{-1}$ the life of the excited states is of the order of 0.01 second. The lives of rotational states may be even longer.

Account must also be taken of the existence of the spins of the nuclei, information about which is yielded by studies of the alternating intensities of the lines in a band of a homopolar molecule.[16] If the two spins oppose each other, the molecule is called symmetrical and if they are in the same direction, it is called antisymmetrical. Wave mechanics indicates the probability of the existence of antisymmetrical hydrogen to be three times that of symmetrical hydrogen. Ordinary hydrogen behaves as a mixture of two gases. The discovery of the existence of this mixture was a spectacular outcome of the work on band spectra. At very low temperatures all of the hydrogen is in the symmetrical form. Bonhoeffer and Harteck have found charcoal to act as a catalyst for the conversion of one form to the other. The two forms have different specific heats and the change in the proportion of the two effected in the presence of the catalyst can be demonstrated by a change in the heat conductance. The antisymmetrical form has been denoted ortho- and the symmetrical form as para-hydrogen. In hydrogen at room temperatures, there is three times as much ortho- as para-hydrogen. The existence of these two forms of hydrogen was predicted by Heisenberg[17] and by Hund.[18] Bonhoeffer and Harteck later made detailed studies of the physical properties of the two forms.[19] Adsorption on charcoal at liquid air temperatures gives practically pure para-hydrogen.

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[16] Mulliken, R. S., *Trans. Faraday Soc.*, **25**, 634 (1929).

[17] Heisenberg, W., *Z. Physik*, **41**, 239 (1927).

[18] Hund, F., *Z. Physik*, **42**, 93 (1928); see also Dennison, D. M., *Proc. Roy. Soc.*, **115**, 483 (1927).

[19] Bonhoeffer, K. F., and Harteck, P., *Naturwiss.*, **17**, 182, 321 (1929); *Z. physik. Chem.*, **4B**, 113 (1929); **5B**, 292 (1929); see also Eucken, A., and Hiller, K., *Ibid.*, **4B**, 142 (1929).

Isotopes in Band Spectra. Since different isotopes of an element have different masses, the momenta of inertia of molecules containing different isotopes should be different. As a result, the bands in the visible or ultraviolet due to molecules some of which have one and others another isotope will be characterized by a duplication of the lines. The bands themselves are also split and superposed.

The existence of isotopes of carbon (13), nitrogen (15), oxygen (17) and of certain other elements were predicted from the data of spectroscopy before they were found by the use of the mass spectrograph of Aston. The oxygen isotope (18) was detected in this manner by Giauque and Johnston in 1929. In the electronic band spectra of isotope mixtures, there is a splitting of the zero position of the bands due to an electronic shift between "vibrationless" states. Its existence implies that the "non-vibrating" molecule is actually in vibration since two isotopic molecules in this state are energetically different. The occurrence of this phenomenon makes certain the existence of a "zero-point" energy of vibration and accounts for the use of $(v + \frac{1}{2})$ in the succession of vibrational terms used in the formulas for the zero lines of bands.

Attempts have been made to effect a separation of isotopes by photochemical means. Kuhn and Martin[20] irradiated phosgene with monochromatic light (2816.179A) obtained from an aluminum arc by the use of filters, and found that the liberated chlorine showed a slight excess of Cl^{35}. Zuber[21] effected a partial separation of the isotopes of mercury by photoöxidation by the aid of a filter which transmitted only the hyperfine components of a spectral line capable of exciting only certain isotopes.

This brief review of the nature and structure of molecular spectra is intended only to serve as an indication of their importance in yielding data of fundamental significance to many branches of chemistry. In the detailed discussion of photochemical reactions in the remainder of the book we shall be concerned with molecular spectra only in so far as they yield information regarding the stability of a photochemically reacting molecule. When by the absorption of energy a molecule is raised to successively higher and higher vibrational states, it may be made to dissociate when the requisite amount of energy has been absorbed. Usually, however, for a vibrational state producing dissociation to be obtained by a molecule absorbing in its ground state, quanta great enough to produce an electronic transition are required. The electron shift alters the binding of the atoms in such a manner that the excited molecule upon the simultaneous acquisition of the requisite amount of energy may be raised to a vibrational state which leads to its dissociation. This is the most frequently occurring primary process in photochemical reactions. The applications of band spectral data to the interpretation of photochemical processes will be considered in more detail in the following chapter.

The following are sources of information on band spectra for readers desirous of obtaining a more thorough discussion, including the mathematical treatment, of band spectra.

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Chapter 14

Spectroscopic Evidence for Dissociation as the Primary Photochemical Process

It is now necessary to consider the manner in which the stability of a molecule sets a limit to the amount of vibrational energy which it can absorb and still remain a molecule. The guiding principle is that a molecule either in the ground state or, as is more commonly the case, in one of its electronically excited states, cannot absorb more vibrational energy than corresponds to its work of dissociation without falling apart into atoms or, if it is a polyatomic molecule, into atoms and free radicals, or two free radicals.

The present viewpoint may be said to have taken its origin from the work of Franck on the dissociation of molecules by electron impact. Blackett and Franck[1] found experimentally that a hydrogen molecule can be decomposed by one collision, a continuous spectrum appearing at the same time. They suggested that the first effect of the collision is to raise an electron suddenly to a higher level. In this new configuration there is a large repulsion between the nuclei great enough to split the molecule into a normal atom and an excited one, both atoms having high velocity. Franck[2] extended the concepts derived from these experiments to an interpretation of photochemical dissociation. In this case the excitation of the molecule and its resultant dissociation are produced, not by a collision with a rapidly moving electron, but the absorption of a quantum $h\nu$ equal to or greater than the work of dissociation of the molecule. If the separation of the atoms during a vibration becomes great enough to overcome the binding force between the nuclei, the atoms may fall apart. It was, however, well known that quantities of energy larger than the work of dissociation may be absorbed by molecules without destroying them. Franck explained this by showing that in such cases not all of the absorbed energy is available as vibrational energy. Instead, a large part of the absorbed energy is consumed in raising the electron system to a higher quantum state, the remaining energy being available only for changing the vibrational and rotational states. Since the rotational quantum is but small, the effects of a change in rotational energy may be neglected. The problem may thus be reduced to that of the stability of the molecule in its various electronically excited states with respect to vibrational energy. Franck prepared potential energy diagrams in which the potential energies of the vibrating atoms are plotted as ordinates against the separation of the atoms as abscissae. Before considering these curves and their relation to spectroscopy, it may be simpler to consider the manner in which molecular spectra indicate the occurrence of dissociation.

INTERPRETATIONS OF CONTINUOUS REGIONS IN SPECTRA

In Chapter 2, it was stated that in atomic spectra the lines of a series converge to a limit. On the short-wave side of this limit the spectrum is continuous. This was interpreted as indicating the separation of an electron from an atom, the latter thereby becoming an ion. The absorption is continuous rather than discrete because the motion of the electron on leaving the atom is not quantized. The velocities with which the electrons are ejected from the various atoms present in the absorbing gas vary continuously and are not limited to definite values. Non-quantized energy levels correspond to non-periodic movements. During the process of ionization the electron changes its motion from a periodic one in an orbit to a non-periodic one in the hyperbolic path which carries it away from the ion. When at a sufficient distance from the ion the electron moves in practically a straight line. It may have any kinetic energy depending upon the amount by which the particular wave-length absorbed exceeded in energy the amount required for the ionization. Since in the light producing the ionization there may be present quanta varying almost continuously in magnitude, atoms absorbing any quantum, A, more than sufficient to produce ionization, will give kinetic energy to the electrons and the ions corresponding to the excess energy. But atoms ionized by quanta corresponding to a wave-length infinitesimally near to that corresponding to A will produce electrons having an infinitesimally greater kinetic energy. Thus when a wave-length band of energy greater than that required to produce ionization is absorbed, the electrons produced will be endowed with continuously varying kinetic energies. Thus it is that in atomic line spectra a continuous region beginning at the convergence limit of a series marks the frequency which corresponds to the work of ionization.

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[1] Blackett, P. M. S., and Franck, J., *Z. Physik*, 34, 389 (1925).

[2] Franck, J., *Trans. Faraday Soc.*, 21, 536 (1926).

A similar ionization of a diatomic molecule can occur but is rarely of photochemical significance. Before ionization of the molecule could be attained, the energies required would be usually more than sufficient to break the molecule into atoms. The effect of dissociation upon the appearance of the spectrum is, however, similar to that of ionization.

Before dissociation, the atoms of a molecule are vibrating to and fro on the line joining their nuclei. With increasing increments of vibrational energy they are separated more and more widely at each oscillation. When the separation becomes great enough the restoring force between the atoms becomes reduced to zero, the vibratory motion between the atoms ceases, and the atoms become separated. Since the kinetic energies with which the atoms move are not quantized, the absorption spectrum becomes continuous at wave-lengths shorter than that which corresponds energetically to dissociation. It must be noted that the molecule which dissociates rarely is in its ground electronic state. Therefore, the energy of dissociation need not be expected to coincide with that required for thermal dissociation. The wave-length at which the spectrum becomes continuous represents the convergence limit of a series of vibrational states of the dissociating molecule in the electronic state from which dissociation occurs. Dymond[3] found a continuous range in the absorption spectrum of iodine vapor. Bonhoeffer and Steiner,[4] as well as Tingey and Gerke,[5] reported a continuous region in the absorption spectrum of hydriodic acid.[6]

Corroboratory evidence for the theory that a region of continuous absorption implies dissociation was soon forthcoming from measurements of the fluorescence of vapors at low pressures. It was stated in Chapter 12 that when the pressure is low, so that collisions are rare, excited molecules re-emit their excitation energy as fluorescence after a period of about 10^{-8} second. Dymond,[7] observed this fluorescence in iodine vapor excited by the absorption of long wave-lengths. But when the absorbed light had only wave-lengths less than about 5000A, the region in which continuous absorption begins, this fluorescence could no longer be observed, an indication that the molecules were no longer present and so could not reëmit their energy of excitation. Similar observations were reported by Bonhoeffer and Farkas.[8] The fluorescence test for dissociation is limited to very low pressures of gas or vapor, since when the pressure is high deactivating collisions become frequent and might remove the excitation energy and so extinguish fluorescence even though dissociation by direct absorption did not occur. Errors due to the emission of radiation as a result of the recombination of atoms to form molecules rarely arise, since, as has been noted in Chapter 13, free atoms rarely combine to form molecules with the emission of their excess energy.[9]

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[3] Dymond, E. G., *Z. Physik*, **34**, 553 (1925).

[4] Bonhoeffer, K. F., and Steiner, W., *Z. physik. Chem.*, **122**, 287 (1926).

[5] Tingey, H. C., and Gerke, R. H., *J. Am. Chem. Soc.*, **48**, 1838 (1926).

[6] See also Leifson, S. W., *Astrophys. J.*, **43**, 73 (1926), for other gases.

Other types of experimental evidence have been advanced to support the theory of direct dissociation. One method employs identification of the resulting free atoms by their characteristic absorption lines. Iodine atoms absorb the 1830.4A line strongly, but iodine molecules do not. Turner found that iodine vapor when irradiated by a carbon arc shows an increased absorption of this line, indicating the presence of iodine atoms. Senftleben[10] demonstrated that excited mercury atoms can dissociate hydrogen. The dissociation was measured by change in the heat conductivity of the gas by a method dependent upon a change in resistance of a wire kept in the gas. With Germer, he extended the method to show the direct dissociation of the halogens on irradiation. That the energy absorbed in excess of that required for dissociation appears as kinetic energy of the atoms was demonstrated by Hogness and Franck[11] for the case of sodium iodide vapor at 650°C. The dissociation yields a normal iodine atom and an excited sodium atom, the latter spontaneously emitting the sodium D line. The Döppler effect (shift in wave-length of the light from a moving source) was utilized to secure information as to the kinetic energy of the sodium atom when produced by the dissociation of the sodium iodide vapor by various wave-lengths within the region of continuous absorption. The Döppler effect was measured by the relative transmission of the emitted light by a layer of sodium vapor, which can only absorb the D line When the dissociation was effected by a silver arc giving effective intense radiation only in the neighborhood of 2450A, 80 per cent of the emitted light was absorbed by sodium vapor. When the dissociating source was a cadmium arc emitting shorter wave-lengths (capable of giving more kinetic energy to the dissociated atoms), only 76 per cent of the emitted light was absorbed by the sodium vapor. With the still shorter radiations of a zinc arc (2139-2026A), the Döppler effect was increased to such an extent that but 50 per cent of the emitted light was absorbed. In this way it could be shown that the kinetic energy of the liberated atoms increases as the frequency of the irradiating light is increased beyond a limit corresponding to 2450A.

Polyatomic molecules, as water, methanol and methyl cyanide, when decomposed by radiations within the Schumann region give rise to excited free radicals, such as OH and CH, which spontaneously emit characteristic bands.[12] Still other lines of direct evidence for the liberation of free atoms and free radicals, such as the conversion of para-hydrogen to ortho-hydrogen, and the effects of free radicals on metallic films, have been advanced. There is now general agreement that photodissociation in a single act of absorption may occur as a result of a primary absorption process. In the case of the reactions of gases which contain a small number of atoms, the nature of the absorption curve of the gas affords a reliable criterion for the occurrence of dissociation. When the absorption lies within a continuous region, the result is dissociation. In the case of very complex gaseous mòlecules containing more than about six atoms, the evidence from spectroscopy is less definite, since the banded region is not well marked in their spectra. In reactions conducted in solution, absorption curves afford little or no evidence regarding the nature of the primary process. (See Chapter 20.)

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[7] Dymond, E G., *loc. cit.*

[8] Bonhoeffer, K. F., and Farkas, L., *Z. physik. Chem.*, **132**, 235 (1928).

[9] Kondratjew, V., and Leipunskiĭ, A., *Z. Physik*, **50**, 366 (1928); **56**, 353 (1929); *Trans. Faraday Soc.*, **25**, 736 (1929).

[10] Senftleben, H., *Z. Physik*, **32**, 922 (1925).

[11] Hogness, T. R., and Franck, J, *Z. Physik*, **44**, 26 (1927).

[12] Terenin, A., and Neuĭmin, H., *Nature*, **134**, 255 (1934).

Franck's Potential Energy Curves

In his Faraday Society paper, Franck visualized the distinction between the dissociation of excited states of molecules and their stability in the ground state by the aid of the potential energy diagrams reproduced in Figure 106. In each of the three diagrams, the lower curve applies to the ground state of a molecule and the upper curve or curves to various electronically excited states. The differences between the upper and lower curves are intended to illustrate the manner in which the change in electron configuration alters the stability of the molecules. To understand the nature of a single one of these curves, it is simplest to consider first the discussion of the meaning of the curves as described by Rabinowitsch in a paper on the interpretation of band spectra.[13]

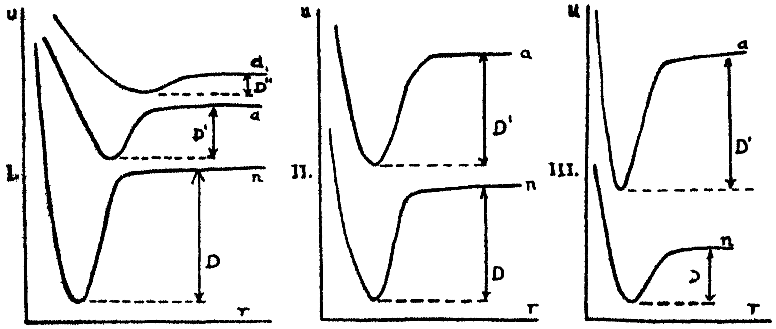

Figure 106. Potential Energy Diagrams of Franck *(Transactions of the Faraday Society).*

It was stated in Chapter 13 that for the pure harmonic oscillator,

$$K = -az$$

This means that the restoring force during an harmonic oscillation is proportional to the displacement z on either side of an equilibrium separation of the atoms of a diatomic molecule. Integration yields the potential energy:

$$P = \frac{az^2}{2}$$

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[13] Rabinowitsch, E., *Z. Elektrochem.*, **37**, 91, 370 (1931).

This is the equation of a parabola (Figure 107) with its two branches meeting at $z=0$, the equilibrium distance between the nuclei, r_0, being measured from the origin. During a vibration from the point of greatest separation of the atoms, the potential energy follows the course of the curve. When the atoms are far apart the attractive forces of valence require that there be a great potential energy. As they move toward each other, this becomes transformed into kinetic energy. At the equilibrium point the potential energy is zero, all the energy being kinetic. As the kinetic energy carries the atoms closer together, the energy again becomes potential because the repulsive forces of the nuclei tend to keep the atoms from coming together. The position of equilibrium (determined as described in the previous chapter from rotational term separations) depends upon the relative magnitudes of the attractive and repulsive forces of the atoms. If the molecule possesses energy denoted by A on the ordinate, a line parallel to the abscissa drawn through A would cut the curve in two places. These determine the distances between the atoms at the extremes of its vibrations when it possesses this amount of potential energy. At these distances from the equilibrium position the total energy of the molecule is potential; there is no kinetic energy. The atoms, changing their directions, are momentarily at rest with respect to each other. At any other distance between the atoms, as for example, at A', part of the energy is potential and part kinetic. By dropping a perpendicular from this point to the abscissa, it is evident that the relative fraction which is potential is given by the ratio $BP:BA'$. Since the vibrational states of the molecule are quantized, the potential energies of the molecule in its permitted states are obtained by drawing a series of equally spaced lines parallel to the abscissa. The extremes of separation of the atoms in each of these vibrational states are given by the points at which each of these lines cuts the curve. The equal spacing of the lines corresponds to successive integral quantum numbers.

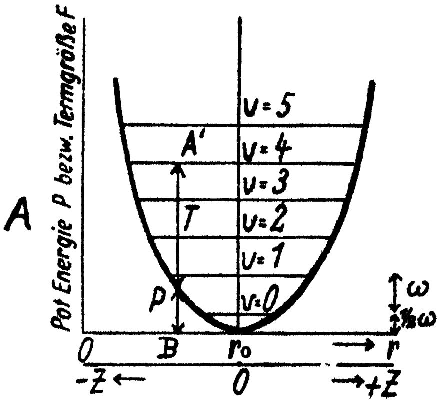

FIGURE 107.

Potential Curve and Vibrational Terms for Harmonic Vibrator (Rabinowitsch, *Z. Electrochemie*).

Z = Elongation
r = nuclear separation
$Z = r - r_0$

It is to be especially noted that the first of these, the so-called "vibrationless state" is so drawn as to indicate that even in it the molecule is vibrating with one-half the energy corresponding to its fundamental frequency. It may be recalled that account was taken of this "zero-point energy" in the equation for expressing the wave numbers of vibration band zero lines in terms of a transition between states. (Chapter 13.)

Since real molecules are not harmonic oscillators, certain changes must be made in the form of the potential energy curve, which nevertheless retains its parabolic form near the equilibrium point. The value of x, the anharmonicity factor in the expression for a vibrational term $F_v = (v+\frac{1}{2})\omega - (v+\frac{1}{2})^2 x\omega$ yields the deviation from the ideal curve to a first approximation. The deviations really result from the necessity for the use of terms in higher powers in the expression for the force of attraction of the oscillator. The effects of the deviations from harmonic oscillations are such as to make the repulsive forces increase more rapidly than linearly as the atoms approach each other, so that the left branch of the curve must be steeper than that of a true parabola. The attractive force no longer increases regularly with the separation. Instead, it attains a maximum at a certain distance of separation of the atoms, after which it becomes smaller and the right-hand branch of the curve changes direction, and finally, at a certain separation of the atoms asymptotically becomes parallel to the abscissa. (See the lower curves of Figure 106.) This means that the atoms no longer attract each other, so that, after attaining a certain separation, they may move away from each other independently and the molecule is dissociated. The value of the energy at which the curve becomes horizontal represents the energy required for dissociation.

In the schematic curves drawn by Franck to illustrate the behavior of various hypothetical molecules (Fig. 106), a deep curve such as I(normal), represents a stable molecule, since the dissociation energy is great. One such as III *n* is not nearly so stable, since the dissociation energy is less. The minima for the curves of the excited molecules are situated at heights which represent the electronic (and rotational) energies of the non-vibrating electronic states. The energy for the dissociation of the excited molecules is measured only from the potential energy of their minima. To dissociate such an excited molecule photochemically would require in addition to this energy, the energy required to form the excited state from the original ground state.

The various curves illustrate the fact that the excitation of a molecule may either weaken, strengthen or leave unchanged the binding strength of the atoms in the ground state. In I, which shows curves for a molecule in its ground state and in two excited states, a, a', the excitation progressively weakens the binding force. Not only does the energy of dissociation lessen, but since the attractive force is weakened, the separation of the atoms at equilibrium also becomes progressively greater with successive states of excitation. Should the absorption of light which produces the electron transition be represented by drawing a vertical line upwards from the minimum of the curve for the ground state, it would strike the curve for the first excited state at a point indicating a potential energy greater than that (D') required to dissociate the excited molecule. Its atoms would, therefore, fly apart as the vibration traced the curve for the excited state. This type of molecule is encountered in the halogens.

The second part of the figure illustrates the case in which the strength of the binding is independent of the state of excitation.

Section III indicates the case in which the binding is made firmer by excitation, so that the moment of inertia is reduced. Examples are such loosely bound molecules as Cd_2 or Zn_2 for which the heat of dissociation is of the order of less than one kcal.[14]

If in such potential energy curves, the horizontal energy levels for the terms corresponding to the successive quantum numbers are drawn in, as in Figure 107 for the harmonic oscillator, the first two or three would be widely and approximately equally spaced. But with successively higher quantum numbers, they become more and more closely spaced (Figure 108), eventually converging at the level at which dissociation occurs. In comparatively few molecular spectra, notably chlorine and iodine, is it possible to trace the convergence of a large number of bands to a limiting frequency which indicates a heat of dissociation.

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[14] Winans, J. G., *Nature*, 123, 279 (1929); *Phil. Mag.*, 7, 555 (1929).

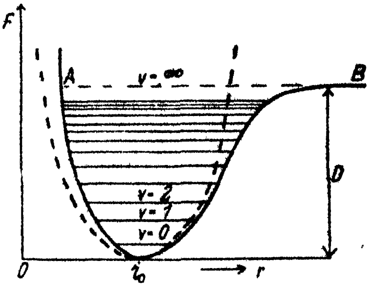

FIGURE 108.

Potential Curve and Vibrational Terms for Anharmonic Vibrations (Rabinowitsch, *Z. Electrochemie*).

In most cases, the bands become weak while still far from the convergence limit and only a limited number of the vibration quanta can be measured directly. Birge and Sponer [15] devised a method of extrapolation to obtain the convergence point.

From the separations of two or more bands, $\Delta\nu = \omega_0(1 - 2vx)$ it is possibly to derive values of the fundamental frequency of the molecule ω_0 and of its anharmonicity x. From these, it was believed that all higher terms might be obtained on the assumption that $\Delta\nu$ is a linear function of v, decreasing as the quantum number increases. At the convergence limit, where $\Delta\nu$ is zero, v is given by $1/2x$. The total energy absorbed is then the integral of ΔF_v between the limits $\nu = 0$ and $\nu = 1/2x$ or $\omega/4x - \omega/2$. To this there must be added the zero-point energy $\omega/2$, so that the heat of dissociation would be equal to $\frac{hw}{4x}$. For a graphical solution, $\Delta\nu$ could be plotted against v and extrapolated to $\Delta\nu = 0$, that is to $v = 1/2x$, the area under the curve giving the heat of dissociation.

Application of this method gave results for the heat of dissociation which in many cases were far too high in comparison with values obtained from thermochemical data. It came to be recognized that the equations employed were not strictly valid and that the results were frequently uncertain when but few vibrational bands could be measured and employed in the extrapolation. Near dissociation, the drop in the separation of the vibrational bands often seemed to be accelerated. Birge [16] modified the extrapolation methods. In the method suggested by Birge, ω_v is plotted against the energy of vibration. $E\omega_v = \Sigma\omega_v$. By the use of the improved method the following values for the heats of dissociation of various gases (expressed as electron-volts) were obtained: N_2 9.1, O_2 6.0, NO 6.6, CO 10 3 [17]

Although Franck said little in his Faraday Society paper as to the manner in which the potential energy curves were obtained, the fertility of the concepts they expressed and their value in the interpretation of the various types of photochemical mechanism were quickly appreciated. Condon [18] devised methods of treating the curves more quantitatively from the standpoint of quantum mechanics and used them in explaining the distribution of the intensities of the lines encountered in band spectra. He conceived an electron transition to occur with such extreme rapidity that the light electron moves to its new orbit in a time so brief that the heavier and more slowly moving nuclei undergo practically no change in position or velocity during the transition. This may be indicated by drawing a vertical line joining the curves for the ground and excited states of the molecule. The transitions occur with the greatest probability from the end points of greatest extension and compression of the molecule where the velocities of the atoms are least. Accordingly the bands corresponding to transitions from the points of reversal of the vibration have the greatest intensity. Strictly the method is not exact since the Heisenberg uncertainty principle shows that it is impossible to know simultaneously the positions and velocities of the nuclei. The error introduced is, however, eliminated by treatment by the methods of wave mechanics.

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[15] Birge, R. T., and Sponer, H., *Phys. Rev*, **28**, 259 (1926). Other methods of evaluating heats of dissociation from the long-wave limits of continuous spectra and from predissociation spectra are ocsasionally employed but cannot be discussed here.

[16] Birge, R. T., *Trans. Faraday Soc.*, **25**, 707 (1929).

[17] For the application of the Birge-Sponer method to the determination of the heats of dissociation of organic compounds from their infrared absorption curves, see Ellis, J. W., *Phys. Rev.*, **33**, 27 (1929).

[18] Condon, E. U., *Phys. Rev.*, **28**, 1182 (1926); **32**, 858 (1928); *Proc. Nat. Acad. Sci.*, **13**, 462 (1927).

If the vertical cuts the curve for the excited molecule at a point deeper than its horizontal asymptote, the absorption spectrum will be predominantly banded, since vibration is possible. But if the curve for the excited state be cut at a point corresponding to a potential energy greater than that of the asymptote, the absorption will be predominantly continuous.[19] It must be noted that there may be several excited states for which separate curves must be constructed.

It is possible to derive the shape of the Franck-Condon curve for a diatomic molecule from a knowledge of three constants of the molecule, r_0, ω and D by means of an interpolation formula due to Morse,[20]

$$F = D'e^{-2ax} - 2D'e^{-ax}$$

in which $a = \sqrt{\dfrac{8\pi^2 c\mu\omega x}{h}} = 0.2454\sqrt{M\omega x}$, μ being the reduced mass in c.g.s. units and M its value in atomic weight units; x is the elongation or the distance from the normal equilibrium nuclear separation r_0, the value of which for a given vibrational quantum number is derived from an analysis of the band spectrum. D' is the heat of dissociation derived thermochemically or by a Birge-Sponer extrapolation.[21] Such curves have been obtained for a large number of molecules and the curves play an essential role in theories regarding thermal reaction rates.[22]

Despite the many difficulties inherent in treating polyatomic molecules, Franck, Sponer and Teller [23] believe that potential energy curves may be profitably employed, at least in qualitive discussions of predissociation.

EXCITED ATOMS FORMED BY DISSOCIATION

Early efforts to test the dissociation theory by comparing the heats of dissociation determined spectroscopically and thermochemically indicated discrepancies; these for a time led certain workers to prefer the theory that the primary process in a photochemical change is more generally one of molecular excitation.

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[19] For quantum mechanical treatments, see Goldstein, L., *Compt. rend.*, **193**, 919 (1931); *J. phys. Radium*, **4**, 123 (1933).

[20] Morse, P. M., *Phys. Rev.*, **34**, 57 (1929).

[21] The calculation of such curves has also been described by Klein, O., *Z. physik*, **76**, 226 (1932). Improved methods have been suggested by others, for which see Sponer, H., "Molekülspektren," J. Springer, Berlin, 1936. Note also Chakravorti, S. K., *Z. Physik*, **109**, 25 (1938).

[22] For further discussion of potential energy curves, see Franck, J., and Sponer, H., *Nachr. Ges. Wiss. Göttingen*, 241 (1928); Visser, G. H., *Chem. Weekblad*, **27**, 237, 380, 390 (1930); Mecke, R., *Physikal. Z.*, **33**, 1 (1932); Noyes, W. A., Jr., *Rev. Modern Physics*, **5**, 280 (1933); Rüdy, R., *Rev. gen. sci.*, **37**, 539 (1926); Heitler, W., and London, F., *Z. Physik*, **44**, 455 (1927); Suguiera, J., *Ibid.*, **45**, 484 (1927); Hylleraas, E., *Ibid.*, **96**, 643 (1935); Finkelnburg, W., *Ibid.*, **99**, 798 (1936).

[23] Franck, J., Sponer, H., and Teller, E., *Z. physik. Chem.*, **18B**, 88 (1932).

That the atoms formed on dissociation of a molecule need not be in the ground state, but that either one or both might be liberated in an excited state was discussed by Franck. If such should be the case it is evident that the apparent value of the heat of dissociation would be greater than the thermochemical value by the energy of excitation. If then the state of excitation of an atom so formed can be determined and if the energy required to raise the atom to that state from the ground state be known, it should be possible to obtain the heat of dissociation from the ground state of the molecule by subtracting the heat of excitation of the atom from the spectroscopic value for the heat of dissociation of the excited molecule.

Iodine may absorb nearly double its dissociation energy and re-emit it as fluorescence without dissociating. From spectroscopic data of Mecke,[24] Franck stated the convergence limit of the vibrational levels of iodine to lie at 4995A. Figure 103 shows that this corresponds to 56,950 calories. Since the thermochemical value for the heat of dissociation of iodine is only 34,500 calories, it is evident that some other process than dissociation of the ground state must be involved in the photochemical dissociation. From the arc spectrum of the iodine atom, its energy of excitation to the $^2P_{1/2}$ state is found to be 21,650 calories per atom. When this is deducted from 56,950 calories, the remainder, 35,300 cal.,[25] is in good agreement with the thermochemical value. The conclusion is, therefore, that the photochemical dissociation of iodine leads to the production of one normal and one excited atom. Similarly, the convergence limit is 4800A for chlorine and for bromine 5107A, each dissociating into a normal and an excited atom.

A normal molecule rarely suffers photochemical dissociation; when it does two normal atoms usually are formed. Herzberg[26] and Heitler and Herzberg[27] have shown that there are instances in which molecules may yield one normal and one excited atom from the ground state, and two normal atoms from an excited state. This is interpreted to mean that a stable molecule is formed by the union of a normal and an excited atom. Instances are CN, BO, SiN, N_2^+, $(CO)^+$. Still other cases have been discussed by Bengtsson and Hulthén, *e.g.*, CuH.[28]

HOMOPOLAR AND HETEROPOLAR MOLECULES

Molecules which, like the alkali halides, yield ions on dissociation from the ground state are called heteropolar or ion-molecules, and those which yield two neutral atoms from the ground state are called homopolar or atom-molecules. In general, atom-molecules such as hydrogen, chlorine, and even such polar ones as silver halides are dissociated from excited states into a normal and an excited atom. Ion-molecules may give both this type of dissociation and one in which only normal state atoms are produced.[29] Franck, Kuhn and Rollefson[30] found the alkali halide vapors to exhibit continuous absorption bands which extend farther toward the red when the temperature and pressure are increased; the position of the maximum absorptions appeared to be independent of these factors. Only one maximum was observed for the chlorides, but there were two for the iodides and bromides. The heats of dissociation of the molecules as calculated from the positions of the longer wave-length continuous bands appeared to be in agreement with thermal heats of dissociation of the salts. Such a conclusion would indicate that it would be possible for ion molecules to be dissociated into two normal atoms.

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[24] Mecke, R., *Ann. Physik,* **71,** 104 (1924).

[25] 35,593 according to Brown, W. G., *Phys. Rev.,* **38,** 709 (1931).

[26] Herzberg, G., *Ann. Physik,* **86,** 189 (1928).

[27] Heitler, W., and Herzberg, G., *Z. Physik,* **53,** 52 (1929).

[28] Bengtsson, E., and Hulthén, E., *Trans. Faraday Soc.,* **25,** 751 (1929).

[29] Sponer, H., *Z. Elektrochem.,* **34,** 483 (1928); Franck, J., and Kuhn, H., *Naturwiss.,* **20,** 923 (1932).

[30] Franck, J., Kuhn, H., and Rollefson, G. K., *Z. Physik,* **43,** 155 (1927).

At low pressures, the vapor of sodium iodide when irradiated with wave-lengths shorter than 2500A emits the D line of sodium.[31] This is proof that the absorption produces an excited sodium atom and an iodine atom. The second series member 3303A only appears when the iodide vapor is irradiated with the 1854-62A aluminum doublet, the energy corresponding to the dissociation energy of the sodium iodide and the excitation of the sodium atom to the 3P state. Since in this process the D line was not emitted, it is not possible that the effects could have been due to an ionization of some sodium vapor possibly present.[32] Similar results were reported by Kondrat'ev[33] for caesium iodide, the dissociation energy of which corresponds to 3.82 volts. The energy required to excite the observed caesium line (4555A) is 2.71 volts. The sum, 6.53 volts, is less than the energy of the aluminum lines 1854 and 1862A which produce the effect, but greater than that of the nickel lines about 2300A, which are ineffective.

In thallium iodide vapor, irradiation with wave-lengths shorter than 2080A leads to the emission of the 3776 and 5351A lines, showing that the dissociation produces thallium in the 2S state; from the result the heat of dissociation into normal atoms would be 61 kcal. per mole.[34] More recently, Terenin and Popov[35] find thallium iodide and bromide to yield thallium and halide ions. Butkov,[36] had previously stated from convergence limits, the heat of dissociation of thallous chloride vapor as 87 kcal. and that of the bromide as 73.1 kcal. Since the decomposition leads to excited atoms, the vapors are atomic compounds.

Neuïmin[37] finds thallous iodide at 600° and 1 mm. pressure to show two absorption bands with maxima at 3110 and 2510A, diffuse toward the long wave side, corresponding to the potential energy curves for $Tl + Cl^*$ and $Tl^* + Cl$. On irradiating these vapors at 100 mm. by a spark, the photodissociation of the salt yields the lines 3776 and 5351A. These atomic lines are not given by resonance in thallium vapors at these temperatures.[38]

Desai[39] found four regions of continuous absorption to be exhibited by the vapors of rubidium iodide. The first, at 3700A, involves a dissociation into normal atoms with an energy of reaction of 78 kcal. The second at 2900A, leads to the production of a normal rubidium and an excited iodine atom, the third at 2548A, to an excited rubidium and a normal iodine atom, and the fourth at 2150A, to the formation of excited rubidium and iodine atoms.[40]

Sommermeyer[41] agrees that the absorption of alkali halide vapors yields only continuous spectra, but finds that by an excitation method he can observe certain bands. Their separation was less at the longer wave-lengths and in the ultraviolet they became progressively feebler and finally disappeared. They correspond with the vibration quantum of the normal state of the molecule, which would be strongly excited at the temperatures used (750°). He suggested that the normal electronic state always corresponded with ionic binding, and the excited state with binding by polarization.

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[31] Kondrat'ev, V., *Z. Physik*, **39**, 191 (1926); Terenin, A., *Ibid.*, **37**, 98 (1926); **44**, 713 (1927); *Naturwiss.*, **15**, 73 (1927).

[32] See also Terenin, A., and Neuïmin, H., *Physik Z. Sowjetunion*, **2**, 434 (1932).

[33] Kondrat'ev, V., *loc. cit.*

[34] Terenin, A., *Z. Physik*, **44**, 713 (1927).

[35] Terenin, A., and Popov, B., *Z. Physik*, **75**, 338 (1932).

[36] Butkov, K., *Z. Physik*, **58**, 232 (1929).

[37] Neuïmin, H., *J. Exp. Theor. Physics, U.S.S.R.*, **4**, 692, 697 (1934); see also Terenin, A., and Popov, B., *Z. Physik*, **75**, 338 (1932).

[38] See also Franck, J. M., *Physik. Z. Sowj.*, **2**, 319 (1932).

[39] Desai, M. S., *Z. Physik*, **85**, 360 (1933).

[40] See also Visser, G. H., and van Heel, A. C. S., *Z. Physik*, **86**, 694 (1933). For alkali fluorides and the heat of dissociation of fluorine, see Desai, M. S., *Bull. Acad. Sci. United Provinces Agra Oudh, India*, **1**, 116 (1931-2); *Chem. Abs.*, **26**, 5842 (1932).

[41] Sommermeyer, K., *Naturwiss.*, **16**, 653 (1928); *Z. Physik*, **56**, 548 (1929).

The absorption of lithium halide vapors has been studied by Desai [42] who found two absorption regions in the vapors of the bromide and iodide. By the use of the ill-defined long-wave limit of continuous absorption, the latent heat of vaporization of lithium was computed to be 29.6 kcal. per g. atom (using the mean value from data on all the lithium halides). On the assumption that the second absorption region corresponds to dissociation into a normal metal and an excited halogen atom, the excitation potentials of bromine and iodine were computed from the frequency difference between the two absorption limits on the long-wave side, giving for bromine 0.46 volt and for iodine 0.91 volt.

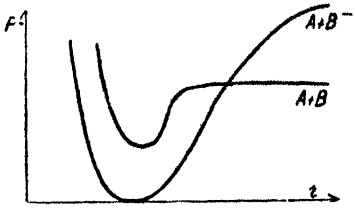

FIGURE 109.

Potential Energy Curves for a Heteropolar Molecule (Rabinowitsch, *Z. Electrochemie*).

Figure 109 illustrates the potential energy curves which characterize a heteropolar molecule. The crossing of the curves is necessary because the energy of a system of two ions must be greater than that of the same two atoms, however excited. The crossing is a point at which the potential energy is the same for a given atomic separation for both the excited and ground states. A molecule at this point may dissociate in either manner so that the molecule cannot be either exclusively homopolar or heteropolar. In some cases the probability of the dissociation following one course exceeds that of its following the other. This is the more likely the greater the energetic separation of the two curves.

It has thus become evident that a simple classification of molecules into heteropolar and homopolar is unnecessary and arbitrary. The view that a given molecule shares the distinguishing features of both types serves to explain the controversy regarding the nature of hydrogen chloride. This was long thought to be heteropolar because of its dissociation into ions in aqueous solutions. Kondrat'ev [43] advanced evidence from the convergence of its infrared bands for a homopolar nature, but Rawlins [44] believed gaseous hydrogen chloride heteropolar because of the constancy of its dielectric constant in a variable magnetic field.[45]

The continuous absorption spectrum of silver iodide vapor closely resembles the spectra of the alkali chlorides.[46] It extends from 3500 to 2400A with a maximum at 3170A. The dissociation results in a normal silver atom and an excited iodine atom. For dissociation into two normal atoms the absorption band would have to be of much longer wave-length. This conclusion was also confirmed by the fluorescence spectrum excited by irradiating the vapor with the copper line 3274A. The heat of dissociation calculated from the fluorescence spectrum is approximately 54 kcal., whereas that found by measuring the work of dissociation is 47 kcal. This indicates that the dissociation products are two neutral atoms and not two ions for which a heat of dissociation of 140 kcal. would be required. In the vapors of silver bromide the absorption bands lie between 3100 and 3400A and for silver chloride between 3100 and 3300A.[47] The vibration frequency changes only slightly between the initial and final electronic states, the difference decreasing from iodide to chloride. A series of resonance lines was obtained by suitable illumination of the vapors. From these the heat of dissociation of silver bromide is roughly estimated at 2.5 volts, in agreement with the thermochemical value, 2.6. This shows that in the vapor state these molecules are non-polar. The true heats of dissociation are closely related to the constants of the quasi-elastic binding forces obtained from the vibration frequency in the normal state. It is therefore concluded that the electron linkage is similar for the three silver halides. Brice[48] finds the absorption of silver bromide and iodide vapors to be continuous below 3350A, with maxima about 3170A for both. The heat of dissociation for the normal states is 2.77 volts (silver bromide) and 3.02 volts (silver iodide), and for the excited states 0.21 and 0.10 volt, respectively. It could not be determined whether the products were metastable halogen and normal silver or metastable halogen and excited silver. Dutta[49] claims the normal form of silver halides in the vapor state to be ionic and not atomic.

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[42] Desai, M. S., *Bull. Acad. Sci. United Provinces Agra Oudh, India*, **2**, 33 (1932); *Chem. Abs.*, **27**, 2380 (1933).

[43] Kondrat'ev, V., *Z. Physik*, **48**, 583 (1928).

[44] Rawlins, F., *Z. Physik*, **50**, 440 (1928).

[45] See, however, Datta, S., and Chakroborti, B., *Current Sci.*, **3**, 349 (1935).

[46] Franck, J., and Kuhn, H., *Z. Physik*, **43**, 164 (1927).

Herzberg[50] has summarized the spectroscopic methods for determining the dissociation energies of diatomic molecules. These methods have been extended to polyatomic molecules. Mecke,[51] who discussed the mechanism of dissociation of molecules such as water, carbon dioxide, methane, formaldehyde and the nitrogen oxides, suggested that that atom is split off first which represents the smallest energy of dissociation.[52]

Terenin[53] observes that the photodecomposition of SnI_4 vapor by light of 2500-2150A is accompanied by a bright visible emission of the spectrum of the iodine molecule with an abnormal distribution of intensity in the bands. The iodine molecule is thought to be detached in one primary process. The whole process is equivalent to a recombination of the atoms in the act of photodissociation, or to a redistribution of the valency linkings. A marked temperature coefficient indicates the necessity for an energy of activation for this type of photodissociation. The mechanism of the yellow fluorescence in the vapor of bismuth iodide may be similarly explained; under the action of suitable quanta and with some thermal activation an iodine molecule may be detached from BiI_3.[54]

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[47] Franck, J., and Kuhn, H., *Z. Physik*, **44**, 607 (1927).

[48] Brice, B. A., *Phys. Rev.*, **38**, 658 (1931).

[49] Dutta, A. K., *Trans Bose Research Inst, Calcutta*, **8**, 248 (1932-3); *Chem Abs*, **29**, 6839 (1935).

[50] Herzberg, G., *Chem. Rev.*, **20**, 145 (1937).

[51] Mecke, R., *Z. physik. Chem.*, **7B**, 108 (1930).

[52] See also Kimura, M, *Sci. Papers Inst Phys. Chem. Research, Tokyo*, **18**, 150 (1932).

[53] Terenin, A., *Nature*, **135**, 543 (1935); *Compt. rend. Acad. Sci. U.R.S.S*, **1**, 482 (1934); **3**, 181 (1935); *Brit. Chem. Abs.* **A**, 807 (1935); Terenin, A., and Tshubarov, R, *Acta Physicochim U.R.S.S.*, **7**, 1 (1937); *Chem. Abs.*, **32**, 3266 (1938); Parti, Y. P., and Samuel, R., *Proc. Roy. Soc*, **49**, 568 (1937); see also Herzberg, G., and Teller, E., *Z. physik. Chem*, **21B**, 410 (1933)] and van Manen, B., *Chem. Weekblad*, **34**, 549 (1937)] for polyatomic molecules.

[54] See also Neuïmin, H., *Physik. Z. Sowjetunion*, **2**, 422 (1932). For zinc and cadmium halides, see Deb, S., *Trans. Bose Research Institute, Calcutta*, **10**, 223 (1934-5); *Chem. Abs*, **32**, 3263 (1938).

In the Schumann region, many molecules of inorganic or simple organic compounds become fluorescent because of dissociation into radicals, some of which are excited.[55] It is, however, unnecessary to discuss in detail the many contributions of spectroscopy to the heats of dissociation of inorganic compounds. The most accurate recent values for the heats of dissociation of various compounds as obtained by all available methods have been compared and tabulated by Rossini and Bichowsky.[56] The band spectra of many compounds will be discussed briefly in the consideration of individual photochemical reactions in the remaining chapters.

PREDISSOCIATION SPECTRA

One feature of the band spectra of certain compounds requires special mention. Franck[57] as early as 1925 mentioned band spectra in which the rotational structure, sharp within the bands at longer wave-lengths, becomes diffuse at shorter ones. He gave the interpretation, no longer regarded as correct, that the rotational energy in such cases is actually great enough to dissociate the molecule. Such spectra had been described by Henri and Teves[58] who called them predissociation spectra. By 1929 this type of absorption had been observed in the spectra of more than 40 polyatomic molecules, such as sulfur dioxide, ammonia, nitrogen peroxide, etc. It is not, however, confined to polyatomic molecules, being exhibited by some diatomic molecules. Indeed, it was first discovered in the case of sulfur vapor in the bands of which the rotation lines disappear at 2792A, although the vibrational bands continue to shorter wave-lengths. Figure 110, showing the absorption of nitrogen peroxide, illustrates the phenomenon. In the bands at 2491 and 2459A, the quantized rotation lines are clearly evident, but they have disappeared in the vibration bands at 244/ and 2425A. In some, but not all, cases the region of predissociation is followed on the short-wave side by a region of continuous absorption. In other cases, the diffuse bands are found on both the long- and short-wave sides of bands with definite rotation lines so that a molecule may exhibit more than one region of predissociation.

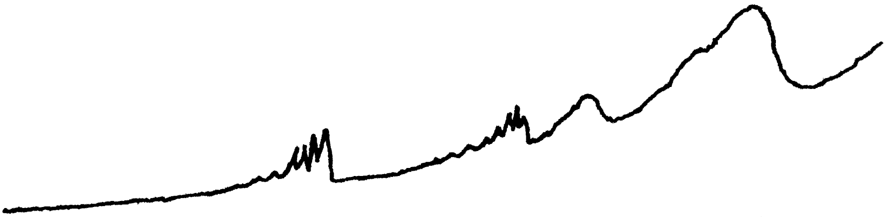

FIGURE 110. Predissociation of NO_2. (Bonhoeffer and Harteck, "Guindlogen der Photochemie," Courtesy, Th. Steinkoff, Dresden).

Henri suggested the name predissociation because he believed that absorption in this region produced a new state of the molecule in which the latter is chemically active, labile, non-fluorescing and predisposed to dissociate. More recent studies have somewhat altered this concept. The interpretation of the phenomenon by the aid of potential energy curves and by the aid of an analogy with the Auger effect in x-ray spectra[59] has been the subject of much work.[60] New criteria for the presence of this type of absorption have been given by Kaplan[61] who has investigated nitrogen spectra.[62]

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[55] Neuimin, H., and Terenin, A., *Bull Acad. Sci. U.R.S.S., Classe sci. math. nat., Ser., phys.*, 529, 1936; *Chem. Abs.*, 31, 3790 (1937)

[56] Rossini, F. D., and Bichowsky, F. R., "Thermochemistry of Chemical Substances," New York, Reinhold Publishing Corp., 1936.

[57] Franck, J., *Z. Elektrochem.*, 31, 350 (1925).

[58] Henri, V., and Teves, M. P., *Nature*, 114, 894 (1924); *Compt. rend.*, 179, 1156 (1924).

In brief, it may be said that the phenomenon depends upon the existence of two excited states of the molecule the potential energy curves for which cross at a position which represents binding for one state and dissociation for the other. In Figure 111, the ground states are not represented for the molecules considered. In each case transitions from the ground state to excited state A are permitted but those to excited state C are forbidden. Assume that by the Franck-Condon principle the electron transition has raised the energy to the points marked X.[63] If only the state C existed, the molecule would suffer dissociation either immediately or after completing a half vibration. If, on the other hand, only the states A were possible, excited molecular states would result and these would account for the production of bands with rotational fine structure. After a brief life (10^{-8} second), they would emit part or all of their excitation energy as fluorescence. But when,

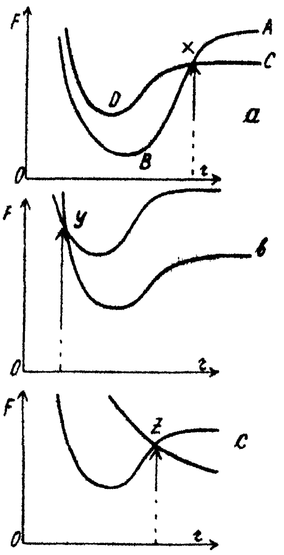

FIGURE 111.

Potential Energy Curves for Predissociation (Rabinowitsch, *Z. Electrochemie*)

as in the figure, two crossed excited states may exist, the molecule may vibrate along either curve. Thus a molecule if excited may during its life of 10^{-8} seconds perform many vibrations the period of which is of the order of only 10^{-13} second before it emits its energy as fluorescence. While it remains as a molecule, it is also rotating and a rotational line (or lines from different ones of the many molecules) is produced within the vibrational band. But during each time that, in the course of a vibration, it passes through the crossing point, the excited molecule stands a finite chance of changing by a "radiationless transition," which involves no change in potential energy, to curve C which leads to dissociation. Thus it is that a single electronic transition gives (in the case of some of the molecules) rotational lines within a vibrational band while other molecules suffering the same electronic excitation undergo dissociation.

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[59] Bonhoeffer, K., and Farkas, L., *Z. physik. Chem.*, **134**, 337 (1927)

[60] Herzberg, G.: "Die Predissoziation und verwandte Erscheinungen," Springer, Berlin (1931), *Phys Rev.*, **40**, 313 (1932).

[61] Kaplan, J., *Phys. Rev.*, **38**, 1079 (1931).

[62] Kaplan, J., *Phys. Rev.*, **41**, 114 (1932).

[63] Franck, J., and Sponer, H., *Nachr. Ges. Wissen. Göttingen*, 241 (1928).

The width of each line of a spectrum is dependent upon the life of the excited state. In general, the longer the life, the narrower the line.[64] The net result of the dissociation of some of the molecules is to shorten the mean life of the excited molecules; the effect of this is to broaden the rotational lines of the absorption band. Because of this tendency the vibrational bands assume the diffuseness characteristic of predissociation. A second effect is a lessening of the intensity of the fluorescence. Fluorescence measurements offer an even more sensitive criterion for predissociation than does the effect of line-broadening although this test can only be used in gases at low pressures. Otherwise the fluorescence might be greatly affected by collisions.[65]

There are "selection rules" concerning the states which may exhibit predissociation,[66] but their consideration would lead us too far into specialized fields of molecular spectra. From a photochemical standpoint, in which we are primarily interested, the significance of the predissociation regions is that they represent regions of optical dissociation and as such are capable of yielding information in regard to the primary photochemical process in the reactions of the substances which exhibit such predissociation regions.

Since in the predissociation region the excitation energy must be at least equal to the dissociation energy, it is possible to calculate a maximum value for the normal heat of dissociation from the wave-length at which the diffuse spectrum commences, or the fluorescence lessens.[67] This can be done only when the horizontal portion of the dissociation curve is cut by the excited curve. As this appears to be the case in numerous instances, such calculations have often yielded heats of dissociation in agreement with those obtained by other methods. The two predissociation limits observed by Henri in nitrogen peroxide at 3700A (NO and O) and 2459A (NO and excited O) correspond to 72.2 and 117 kcal. The difference between these fixes the energy of excitation of oxygen at 45 kcal.[68] Similarly calculations of the heat of dissociation of oxygen have been made from the predissociation spectrum of sulfur dioxide. From predissociation limits, Bates[69] has calculated the heats of dissociation of OH and NH to be 116.05 and 102.2 kcal. Urey and Johnston[70] find the predissociation limit of chlorine dioxide to indicate an energy of dissociation through one mode of vibration of the excited electronic state into a ClO molecule and an oxygen atom.

Predissociation may be induced in certain cases in spectral regions normally showing discrete band spectra, by the addition of other gases. The change of absorption spectrum is practically independent of the nature of the foreign gas, at least in the case of the visible bromine spectrum observed by Avramenko and Kondrat'ev.[71] External magnetic fields may also cause induced predissociation.[72]

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[64] The details of the theory of this relation must be sought in physical texts. The application of the Heisenberg uncertainty principle is involved. See also Rice, O. K., *Phys. Rev.*, **33**, 748 (1929); *J. Chem. Physics*, **1**, 375 (1933) and Kronig, R. de L., *Z. Physik*, **50**, 347 (1928).

[65] Kondrat'ev, V., and Polak, L., *Z. Physik*, **76**, 386 (1932).

[66] Kronig, R. de L., *Z. Physik*, **62**, 300 (1930).

[67] Turner, L. A., *Z. Physik*, **68**, 178 (1931).

[68] See also Herzberg, G., *Z. physik. Chem*, **10B**, 189 (1930).

[69] Bates, J. R., *Z. physikal. Chem. Bodenstein Band*, 329 (1931).

[70] Urey, H. C., and Johnston, H., *Phys. Rev.*, **38**, 2131 (1931).

[71] Avramenko, L., and Kondrat'ev, V., *Physik. Z. Sowj.*, **10**, 741 (1936); *Chem. Abs.*, **31**, 8366 (1937). See also Loomis and Fuller, *Phys. Rev.*, **39**, 180 (1932); Kondrat'ev, V., and Polak, L., *Physik. Z. Sowj.*, **4**, 764 (1933).

[72] Turner, L., *Phys. Rev.*, **41**, 627 (1932).

A general discussion of induced predissociation and the predissociation of polyatomic molecules has been given by Burton and Rollefson.[73]

The principles followed in interpreting the predissociation spectra of diatomic molecules require amplification when applied to the spectra of polyatomic molecules so as to take into account the more complex nuclear vibrations and the fact that polyatomic products of decomposition contain vibrational and rotational energy, while for monatomic dissociation products only electron excitation energy need be considered. In the case of sulfur dioxide,[74] the energy value for the predissociation limit at 1950A is greater than the energy required for thermal dissociation into SO and O by about 13 kcal.; this must be divided between translational and vibrational and even some rotational energy.

A marked shifting of the region of predissociation to longer wave-lengths with increase in the temperature of the absorbing gas was noted by Henri in his work on predissociation. Joos and Hermann [75] have confirmed Herzberg's suggestion that this is due to the thermal excitation of higher vibrational levels in the ground electronic state, by observations on nitrogen peroxide at temperatures from − 15° to 500° These show that the sharpness of the individual bands is not affected by the rise in temperature. The temperature effect is of some significance for the temperature coefficients of certain photochemical changes.

Caution must be used in concluding that photochemical reactions brought about by light absorbed in a region of sharply banded absorption have an excited molecule mechanism,[76] since induced predissociation may occur in molecules showing any kind of light absorption. Furthermore, weak continuous absorption between the lines of a spectrum must not be neglected. Consideration of such absorption in the chlorine spectrum at wave-lengths longer than the convergence limit has led to a recent revision of the interpretation of the mechanism of the combination of hydrogen and chlorine induced by light in this region.[77]

Franck and Rabinowitsch [78] have stated that in the majority of photochemical reactions in gases every act of absorption leads to dissociation into atoms or free radicals, a point of view in which Lowry [79] concurs. West [80] tests for the paramagnetic free radicals by ability of the latter to effect the ortho-para hydrogen conversion. He applied the method with success to the detection of methyl radicals produced by the irradiation of methyl iodide and of acetone vapors. However, benzene and propionaldehyde when illuminated did not cause the ortho-para hydrogen conversion. Neuĭmin [81] uses a layer of molybdenum trioxide in the detection of atomic hydrogen, which forms an intense blue color, "molybdenum indigo."

[73] Burton, M., and Rollefson, G. K., *J Chem Phys*, **6**, 416 (1938). For the case of sulfur, see Olsson, E., *Naturwiss*, **25**, 781 (1937) and Lochte-Holtgreven, W., *Z. Physik*, **109**, 147, 149 (1938).

[74] Franck, J., Sponer, H., and Teller, E., *Z. physik. Chem*, **18B**, 88 (1932). For a general theoretical discussion of the predissociation of polyatomic molecules, see Dushinskii, F., *Acta Physicochim. U.R S.S.*, **5**, 651 (1936).

[75] Joos, G., and Hermann, A., *Physik. Z.*, **33**, 213 (1932).

[76] Rollefson, G K., *J. Phys. Chem.*, **42**, 737 (1938).

[77] Bayliss, N. S., *Trans. Faraday Soc.*, **33**, 1339 (1937).

[78] Franck, J., and Rabinowitsch, E., *Trans Faraday Soc.*, **30**, 120 (1934).

[79] Lowry, T. M., *Trans. Faraday Soc*, **30**, 3 (1934).

[80] West, W., *J. Am. Chem. Soc.*, **57**, 1931 (1935).

[81] Neuĭmin, H., *Compt. rend. acad. sci., U.R.S.S.*, **16**, 447 (1937); *Chem. Abs.*, **32**, 1580 (1938).

Chapter 15

Overall Photochemical Reactions

It has been shown in the preceding chapters that it is advantageous to consider separately the mechanisms of the primary and secondary processes of photochemical reactions. Experimentally, however, there is no such demarcation and both must be studied simultaneously.

It is now generally recognized that for chemical reactions to proceed the molecules must be supplied with at least a minimal amount of energy known as the activation energy. This is usually not identical with the observed heat of reaction, the latter being merely the difference between the activation energies for the forward and reverse reactions. In purely thermal reactions, the activation energy is kinetic energy due to random collisions resulting from the heat motion of the molecules. Only those molecules which at the experimental temperature have energies in excess of the activation energy are capable of reacting. Since from the Maxwell-Boltzmann distribution law at ordinary temperatures only about one in 10^7 molecules of a gas possesses an energy equivalent to 25 kcal. per mole, reactions for which the activation energy is greater than this will be slow. The absorption of ultraviolet light may, however, readily supply the molecules with far greater amounts of energy so that the photochemical reaction may be rapid. Thus, the processes of dissociation or excitation attendant upon the absorption of light may yield atoms, free radicals or molecules with sufficient activation energy to allow the remaining secondary reactions to proceed readily.

Whether or not the secondary reactions do so depends upon the nature of the secondary reactions in which these primary products participate. If all the secondary reactions proceed at the experimental temperatures with negligible activation energies, or with activation energies compatible with those possessed by the primary products, the photochemical reaction will proceed. The rate of reaction is then determined by that of the primary process, which depends upon the rate of absorption of energy. If, on the other hand, the secondary processes require activation energies in excess of those possessed by the primary products the reaction will not proceed. In such cases, the temperature must be raised to one at which the requisite activation energy for the slowest necessary secondary process is available. The overall reaction will then have a temperature coefficient. In general, the primary process is not markedly dependent upon temperature, and purely photochemical reactions have temperature coefficients of unity. This means merely that none of the secondary processes requires activation energy. When there is a temperature coefficient, it is usually due, therefore, to one of the secondary processes requiring activation energy not sufficiently available at the usual experimental temperatures. Since most photoreactions occur through the intermediate formation of atoms and free radicals, an accurate knowledge of the rate constants of reactions in which these participate is of importance for the determination of the mechanisms of individual photoreactions.[1]

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[1] Bates, J. R., *Chem. Rev.*, **17**, 401 (1935).

PHOTOCHEMICAL THRESHOLDS

Since it is the function of light in a photochemical reaction to supply the energy of activation for that reaction (or more strictly for its primary process), it should be necessary to employ a radiation of frequency corresponding to at least that energy. This implies the existence of a photochemical threshold frequency below which the reaction could not be brought about. Mecke[2] states that the accurate determination of this threshold wave-length is important for a proper understanding of the nature of the primary process, but notes that it unfortunately presents great experimental difficulties. Indeed, some workers have indicated these difficulties to be so great as to preclude experimental determination.

In the case of the combination of hydrogen and chlorine, Coehn and Jung[3] claimed to have found a threshold at 5400A, longer wave-lengths not leading to the formation of hydrogen chloride. On the other hand, Taylor[4] placed the threshold at 4900A. Both of these results were criticized by Bowen,[5] who showed that the results indicated no more than that the rate of reaction is proportional to the amount of light absorbed and that this drops to low values in these wave-length regions.

A similar attempt to find critical wave-lengths for the decomposition of ethyl and methyl iodides was due to Job and Emschwiller.[6] They considered the quantum at the critical wave-length for the decomposition (the "critical complement"), to measure the binding energy of the covalence C-I. By placing a tube of ethyl iodide in the spectrum of a carbon arc, it was noted that the reaction appeared to proceed as soon as wave-lengths shorter than 4100A were used. This corresponds (Figure 103) to 69.3 kcal. per mole. Methyl iodide gave this same value, but for iodobenzene it was 4000A or 71 kcal. However, Bowen[7] criticized these conclusions by showing that the threshold values were related either to the lower limits of the absorption spectrum or to the wave-length of maximum absorption. Bowen stated there was no theoretical justification for such conclusions. Warburg had attempted to relate thresholds to the heat of linking. The thermal values for the C-I linking gave only 40 kcal., whereas Job and Emschwiller had found 69.3 kcal. As has been indicated in an earlier chapter the heat of dissociation of such molecules as iodine into normal atoms is not related to the actual amounts of energy required to dissociate the molecule into a normal and an excited atom; this may be far greater. Therefore, heats of linking could not be calculated even from a knowledge of the convergence limit without a knowledge of the amount of excitation energy of the decomposition products. Allmand and Reeve[8] found the decomposition of oxalic and formic acids to proceed at a measurable rate in light of wave-lengths much longer than those computed by Volmar[9] from thermochemical data on the heats of unimolecular decomposition.

Schneider and Sperti[10] suggested the existence of threshold wave-lengths for photochemical reactions. By means of a series of filters they found the longest wave-length capable of liberating iodine from a solution of potassium iodide to lie between 3340 and 3660A. Inasmuch as wave-bands covering as much as 320A units had to be used, it was not possible to determine whether or not the yield dropped suddenly to zero from fairly high values over a very narrow range of wave-lengths. These authors extended their point of view to the inactivation of the enzymes pepsin, rennet and invertase and to the killing of bacteria and protozoa as well.

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[2] Mecke, R., *Trans. Faraday Soc.*, **27**, 360 (1931).

[3] Coehn, A., and Jung, G., *Z. physik. Chem.*, **110**, 705 (1924).

[4] Taylor, W., *Phil. Mag.*, **49**, 1165 (1925).

[5] Bowen, E. J., *Phil. Mag.*, **50**, 879 (1925).

[6] Job, A., and Emschwiller, G., *Compt. rend.*, **179**, 52, 168 (1924).

[7] Bowen, E. J., *Trans. Faraday Soc.*, **21**, 543 (1926).

[8] Allmand, A. J., and Reeve, L., *J. Chem. Soc.*, **129**, 2852 (1926).

[9] Volmar, *Compt. rend.*, **178**, 697 (1924); **180**, 1172 (1925).

[10] Schneider, H., and Sperti, G., *Bull. Basic Sci. Research*, **1**, 7 (1926).

Further tests of the question require accurate determinations of the quantum yields at a series of wave-lengths; a positive threshold would be indicated by a sudden drop to zero from a fairly high and constant quantum yield. Comparatively few such data are available, but those papers in which data adequate to the test have been given, *e.g.*, the work of Norrish[11] on the decomposition of nitrogen dioxide, indicate a sloping curve over a fairly wide range of wave-lengths. For this reaction the quantum yield is zero at 4360A, 0.72-0.74 at 4050A, 1.54-2.10 at 3650A and 2.07 at 3100-2700A. A possible explanation of the lack of sharpness in the change in quantum yield with wave-length may be that not all of the molecules of the absorbing material are initially in the same vibrational state. Those few molecules which at the temperature of the experiment may be in excited states may be expected to be activated by the absorption of smaller quanta than are required to activate those initially in lower vibrational states.[12] The heat of dissociation obtained spectroscopically by the absorption of a gas at a temperature other than absolute zero is the weighted mean of the heats of dissociation of the various vibrational excited states existing at the temperature at which the absorption occurs. Conversely, since these states have different heats of dissociation, the wave-length threshold for each should be definite, but for the mixture there should only be a sloping curve or a diffuse threshold.

By extrapolating the quantum yields of each of four reactions to a zero quantum yield, Rao and Dhar[13] found extrapolated threshold wave-lengths. The corresponding energies in kcals. per mole were found to agree closely with the energy of activation of the dark reactions. There was, however, in some of these a rather extended and uncertain extrapolation. Bowen had found much earlier that the activation energies of four bimolecular reactions calculated from their temperature coefficients could not be related to the energies corresponding to the long-wave limits of the absorption bands. Neither the absorption limit nor the activation energy bore any definite relation to the heats of linking of the bonds assumed to be ruptured in the photochemical processes.

Franck and Herzfeld[14] have emphasized the possibility, at least for polyatomic molecules, that thermal energy can contribute much more of the energy required for a photochemical change than had previously been assumed. Also, in such complicated molecules more than one absorbing center may be present. Energy absorbed by one linking may be transferred to another, which itself absorbs, so that the sum or a portion of the sum of the energies absorbed in separate portions of the molecule may be made available to affect a disruption of one or the other linking, the energy absorbed by that linking alone being insufficient for this purpose. The possibility of such intramolecular migrations of energy seems to have been definitely shown in the work of Norrish on the photochemistry of the aldehydes. (Chapter 22.)

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[11] Norrish, R. G. W., *J. Chem. Soc.*, 1604 (1929).

[12] Tolman, R. C., *J. Am. Chem. Soc.*, **42**, 2506 (1920); **45**, 2285 (1923).

[13] Rao, G. G., and Dhar, N. R., *J. Phys. Chem.*, **36**, 646 (1932).

[14] Franck, J., and Herzfeld, K. F., *J. Phys. Chem.*, **41**, 97 (1937).

Over wide ranges of wave-lengths there may be variations in the quantum yield with the wave-length. In many reactions, the quantum yield increases with the frequency. In the case of the hydrolysis of tetrachlorplatinic acid[15] the yield continues to increase over a range of 3080A, which coresponds to a range of energy levels far too great to be accounted for on the basis of a temperature distribution of vibrational states. The reasons for this phenomenon are not yet clear. Such results appear to be obtained chiefly in reactions involving polyatomic molecules in solution.

TEMPERATURE COEFFICIENTS

Since the secondary processes are thermal reactions, they may be expected to possess temperature coefficients different from unity. Nevertheless, early observations by Eder (1879) and by Goldberg[16] indicated most of the then known photochemical reactions to have temperature coefficients close to unity. Bancroft and Allen[17] disagreed and several reactions with higher values were brought forward by Plotnikow,[18] who proposed to classify photochemical reactions into three groups with temperature coefficients of 1.04, 1.20 and 1.45, respectively. Most reactions were thought to belong to the first group. The second group contained a few reactions in which it was suggested that diffusion processes determined the rate.[19] The third group comprised chiefly those reactions in which halogens were the absorbers. In determining the temperature coefficient, the effects of a possible dark reaction had to be eliminated either by working at very low temperatures and with light of high intensity or by subtracting dark rates determined in separate experiments. This latter step assumed the principle of the additivity of the rates of light and dark reactions, a principle for which there is little present justification.

The data at present available for a large number of reactions[20] show the distribution of temperature coefficients to be random, so that the Plotnikow classification into three groups has lost significance. Furthermore, the idea that the halogens fall into a special class was disproved by Hertel,[21] who found that the temperature coefficient for the hydrogen-chlorine combination has different values when light of different wave-length regions is employed. With light in the region of the band spectrum of chlorine, the temperature coefficient is 1.48, but with light within the continuous region at shorter wave-lengths, it is 1.37. In the presence of traces of oxygen, the true values may be masked, since 1.12 was stated to be the temperature coefficient of the reaction under such conditions.

It was early recognized that the temperature coefficient for a dark reaction should be expected to be higher than for a light reaction.[22] An indication of the relative magnitudes of the light and dark temperature coefficients for a number of reactions was given by Banerji and Dhar.[23] The decomposition of trichloracetic acid has a temperature coefficient of 3.0 in the light and of 4.28 in the dark. For the inversion of cane sugar they give the values 3.4 and 3.82, for the oxidation of sodium nitrite by iodine, 1.4 and 2.5, and for the action between oxalic and hydriodic acids 2.2-2.5 and 2.98 respectively.

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[15] Cited by Style, D. W. G., "Photochemistry," p. 69, Methuen, 1930, from Boll, M., *Ann. Physique*, 25, 243 (1914).

[16] Goldberg, E., *Z. physik. Chem.*, 41, 1 (1903); *Z. wiss. Phot.*, 4, 56 (1906).

[17] Bancroft, W. D., and Allen, R. P., *Proc. Nat. Acad. Sci.*, 15, 445 (1929).

[18] Plotnikow, J., *Z. physik. Chem.*, 78, 573 (1911).

[19] See for certain reactions in liquid systems, Berthoud, A., and Bellenot, H., *J. chim. Phys.*, 21, 308 (1924). Abel, E., and Schmid, H., *Monatsh.*, 61, 361 (1932), find the temperature coefficient of a streaming reaction smaller than that of a quiet one.

[20] For tabulations of temperature coefficients, see Plotnikow, J., "Allgemeine Photochemie," 2nd Ed., de Gruyter, Berlin, 1936. Kistiakowsky, G. B., "Photochemical Processes," New York, Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1928.

[21] Hertel, E., *Z. physik. Chem.*, 15B, 325 (1932).

[22] Bodenstein, M., *Z. physik. Chem.*, 85, 380 (1913).

[23] Banerji, R. C., and Dhar, N. R., *Z. anorg. allgem. Chem.*, 134, 172 (1924); *Chem. Abs.*, 18, 2634 (1924).

Indian workers have devoted considerable attention to such determinations.[24] In general, it has been found that the temperature coefficients of light reactions vary with the wave-length of the incident light, although the coefficients are usually less than those of the corresponding thermal reactions. The greater the extent to which a reaction is accelerated by light, the smaller is the value of the temperature coefficient. Yajnik and Uppal were unable to find any relation between the temperature coefficients and the dielectric constants of the solvents employed.

Temperature coefficients less than unity are very rarely encountered. They could be interpreted as meaning that the temperature coefficient of some dark inhibiting reaction in a chain mechanism is greater than that of the chain-lengthening processes.

The temperature coefficients discussed in the preceding paragraphs are those of the velocities of reactions, the light intensity being held constant. The results recounted have held little general significance. More important theoretically are the results obtained when the amount of absorbed energy is maintained constant and the coefficients are computed for the quantum yields. Such values will differ from those of velocity measurements at constant incident intensity when the measurements are not made under conditions of total absorption if there is a dependence of the extinction coefficient upon the temperature.

In some cases a complex formed in a solution absorbs some of the light, as for example, the triiodide ion in reactions involving oxidation by iodine. In such a case, the light is partly absorbed by iodine and partly by the triiodide ion, only the former being effective. The amount of triiodide ion present depends upon the temperature since the reaction for its formation has a temperature coefficient. Accordingly, the photochemical reaction will have a temperature coefficient for its quantum yield dependent upon a temperature coefficient of the efficient absorption. Such reasoning may conceivably apply also to cases in which solvation of the absorbing molecule plays a prominent part.

But there is a more fundamental sense in which the process of absorption may be attended by temperature effects—there may be a variation of the extinction coefficient of a substance with temperature. Tolman [25] noted the possibility that a molecule might have to be raised to an energy state higher than that of the normal state before it would be capable of absorbing certain radiations. Otherwise stated, the probability of absorption might depend upon the original quantum state of the molecule. There is evidence that the absorption coefficients of gases possess temperature coefficients. v. Wartenberg [26] concluded that the absorption of longer wave-lengths by oxygen at 1800° C. gave evidence of being largely due to molecules possessing a considerable amount of internal energy.[27] However,

[24] Mukerji, B., and Dhar, N. R., *J. Phys. Chem.*, **33**, 850 (1929); Yajnik, N. A., and Uppal, H. L., *J. Indian Chem. Soc.*, **6**, 729 (1929); *Chem. Abs.*, **24**, 1035 (1930).

[25] Tolman, R. C., *J. Am. Chem. Soc.*, **42**, 2506 (1920); **45**, 2285 (1923).

[26] v. Wartenberg, H., *Physik. Z.*, **11**, 1168 (1910).

[27] See also observations on bromine by Ribaud, G., *Ann. Physique*, **12**, 107 (1919), and on chlorine by Dobbie, J. J., and Fox, J. J., *Proc. Roy. Soc.*, **99A**, 456 (1921) and by Kuhn, H., *Z. Physik*, **39**, 77 (1926).

the effects of temperature on light absorption are generally insufficient to account for the temperature coefficients of photochemical overall reactions. Since electronically excited states cannot be excited by thermal means, at least within the temperature ranges usually under consideration, the possibility of getting excited states is limited to that of vibrational states. However, for most gases, the number of molecules in any but the lowest few vibrational levels can usually be neglected. For this reason, the possibility raised by Tolman apparently is not of great practical significance. Young and Style[28] have given a detailed discussion of the manner in which a study of the temperature coefficient of a reaction may give information as to its mechanism. According to Dhar and Bhattacharya,[29] an increase in the absorption of light by a molecule is associated with increased chemical reactivity and a weakening of the binding forces. When a molecule becomes more reactive because of an increase in temperature or the presence of sensitizers it is likely to absorb light more markedly. It has been reported by Dhar and Bhargava,[30] that in certain cases, the light absorption of a mixture of substances may be greater than the sum of the absorptions of the separate substances. The increased absorption is attributed to an activation of molecules by the presence of other molecules. Fast reactions are claimed to show greater light absorption than do slower ones.

It is possible to eliminate the question of temperature effects on absorption when variations in the temperature coefficients do not occur in systems having a wide range of variation of the original concentration of the absorbing component. When effects due to a variation of the primary process with temperature can be eliminated, as is most generally the case, the temperature coefficients of the quantum yields of photochemical reactions give information regarding the mechanism of the secondary processes.[31] As such, they can best be discussed in connection with the individual reactions in which they are encountered. In general, it has been recognized that the temperature coefficients decrease as shorter wave-lengths of light are employed.[32] The use of shorter wave-length light usually gives an increased quantum yield but a smaller temperature coefficient, but exceptions are known.

Most of the sources of a temperature effect of a quantum yield—diffusion, change in viscosity of a solvent, thermal activation of some one of the secondary reactions—would tend to produce definite values of some energy of activation at the temperature of measurements, or else would cause the calculated thermal activation energy for an intermediary process to decrease when determined at higher temperatures. Nevertheless, Kistiakowsky[33] has found in two reactions—the oxidation of hydrogen and that of carbon monoxide, irradiated by an aluminum spark—temperature coefficients which increased with temperature. Style[34] makes the suggestion that in such cases collisions of the products of some highly exothermic secondary reaction with the absorbing molecules may activate the latter, some thermal activation energy being required for this process.

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[28] Young, K. W., and Style, D. W. G., *Trans. Faraday Soc.*, 27, 493 (1931).

[29] Dhar, N. R., and Bhattacharya, A. K., *Z. anorg. Chem.*, 176, 372 (1928); *J. Indian Chem. Soc.*, 11, 33, 311 (1934); *Chem. Abs.*, 28, 3663, 6636 (1934).

[30] Dhar, N. R., and Bhargava, P. N., *Nature*, 134, 848 (1934).

[31] Young, K. W., and Style, D. W. G., *loc. cit.*

[32] Padoa, M., *Atti accad. Lincei*, 25 (II), 168, 215 (1916); 24 (II), 97, 828 (1915); *Gazz. chim. ital.*, 55, 87 (1925).

[33] Kistiakowsky, G. B., *Proc. Nat. Acad. Sci.*, 15, 194 (1929).

[34] Style, D. W. G., "Photochemistry," Methuen, 75, 1930.

KINETICS OF PHOTOCHEMICAL REACTIONS

Many attempts to generalize regarding the rates of photochemical reactions have been made, but these have not proved very profitable because of the great complexity of the individual processes encountered. Conditions affecting the rate of absorption of light introduce many variables not encountered in the study of the kinetics of thermal reactions. The speed of stirring may influence the rate when most of the light is absorbed close to the window through which it enters. Photochemical processes may be aided by, opposed by, or independent of simultaneous thermal processes. The order of a given reaction conducted thermally may differ from that when it is conducted photochemically.

Bodenstein[35] believed the rate of absorption of light to be the principal factor controlling the velocity of photochemical reactions. The concentration of molecules other than the ones which absorb radiation was also recognized as an important factor. The simple law relating the rate of the reaction to the absorbed energy $dx/dt = KI_{\text{abs.}}$ is applicable only when the possibility of the transfer of the absorbed energy to other molecules by collisions is negligible.[36]

Wegscheider[37] developed a series of kinetic expressions based upon the conception that the rate is proportional to the light absorbed in a localized volume of the reaction mixture, rather than to the amount absorbed within the total volume. He extended his mathematical treatment[38] to the velocities of reactions with intermediary formation of excited molecules. Wegscheider believed the intensity of the light to enter the equation for the rate of formation of a product not as the first power, but as a power which gradually decreases to zero as the intensity decreases. The total absorption from the start of the reaction to the exhaustion of the absorbing component might, however, be independent of the intensity. He emphasized the possibility that the quantum yield might vary considerably during the course of a reaction, so that values determined over only a selected time interval might be more or less fortuitous. He noted also that only in cases in which the fate of the excited molecule follows a unimolecular law and the primary process is irreversible should it be expected that the quantum yield would be one. Recently, Wegscheider[39] has treated several systems by taking into account the light absorbed by the solvent and the reaction products as well as by the reacting substances. It is obvious that the secondary processes may be so complex in the individual case and so varied from reaction to reaction that attempts at generalizations in regard to the kinetics of overall reactions are not likely to be successful.

Several workers have attempted to classify reactions into those which are proportional to the first power of the light intensity and into those proportional to the square root of the intensity. From studies of nine inorganic reactions, Bhattacharya and Dhar[40] found two (those between chromic and oxalic acids and between potassium persulfate and potassium iodide) in accord with the first power law. The others were proportional to the square root of the intensity. They believed the latter to be the case for reactions with atomic oxygen as an intermediate. They stated that if the reactants exhibit marked absorption of light, the velocity of the reaction increases in proportion to, or more rapidly than in direct proportion to, an increase in the intensity of the light. For systems with but slight absorption of light, they considered the square root law to be valid. It was found possible in many cases to alter the rate of the dark reaction by the addition of accelerators or inhibitors. By increasing the dark rate and exposing the system to radiation which could be only slightly absorbed, a true photochemical reaction proportional to the square root of the intensity of the incident radiation or to the amount of energy absorbed, could be made to become proportional to the first power of the intensity. On the other hand, a reaction proportional to the incident intensity or to its square could be made proportional to the square root of the intensity by decreasing the velocity of the dark reaction and so increasing the photochemical velocity. These observations were extended by Mukerji and Dhar to include[41] some fifteen pairs of substances. In a few reactions (sodium formate and iodine, Rochelle salt and bromine, the oxidation of quinine sulfate by chromic acid) the rate was proportional to the square of the intensity. No relation was found between the velocity of reaction of oxalic acid with potassium permanganate and the intensity of the incident light. The other reactions studied fell into the two classes described by Bhattacharya and Dhar, who believe all true photochemical reactions (with negligible dark reactions) tend to be proportional to the half or lower power of the intensity of the incident radiation.

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[35] Bodenstein, M., *Trans. Faraday Soc.*, **21**, 525 (1926).

[36] For the dependence of the velocity of a photochemical reaction on the intensity of illumination, see also Gaviola, E., *Anales assoc. quim. Argentina*, **18**, 133 (1930).

[37] Wegscheider, R., *Rec. trav. chim.*, **44**, 1118 (1925); *Z. physik. Chem.*, **103**, 273 (1922).

[38] Wegscheider, R., *Monatsh.*, **51**, 285 (1929).

[39] Wegscheider, R., *Monatsh.*, **62**, 101 (1933).

[40] Bhattacharya, A. K., and Dhar, N. R., *Z. anorg. Chem.*, **175**, 357 (1928); *J. Indian Chem. Soc.*, **6**, 473 (1929).

Cases in which the rate appears to increase more rapidly than the intensity of the light are attributed by Bhagwat[42] to the presence of inhibitors which are relatively less effective in retarding the reaction when the intensity of the light is high. Bhagwat and Dhar[43] also assert that when the reaction velocity is not directly proportional to the light absorption, stirring will tend to increase the rate and decrease the temperature coefficient. However, when the velocity is directly proportional to the absorption, stirring will have no effect on the velocity of the reaction or the temperature coefficient.

Allmand[44] found that if the product of the extinction coefficient and the thickness of the absorbing layer is very small, the quantum efficiency for any wavelength is inversely proportional to the square root of the rate of energy absorption. If the thickness of the absorbing layer is continuously increased from a very small value until it becomes great enough to make the absorption of the incident energy complete, the limiting value of the quantum efficiency is twice as great as that in thin layers.

Recent work on chain reactions has indicated that in general the square root relation may be expected if the substance which acts as intermediary in carrying the chain is formed at a rate proportional to the intensity, but does not hold when the intermediary substance is formed at a rate proportional to the square of its concentration.[45] Since in many reactions the chains are carried by atoms liberated in the primary process and since these atoms are removed by three-body collisions involving two atoms, the first-mentioned conditions are frequently met. This accounts for the number of reactions for which the square root law has been found to hold with a fair degree of approximation. Bhagwat[46] believes the square root relationship is more likely to be observed in the region of high frequencies than in that of lower ones.

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[41] Mukerji, B. K., and Dhar, N. R., *J. Phys. Chem.*, **32**, 1308 (1928).

[42] Bhagwat, W. V., *J. Indian Chem. Soc.*, **11**, 443 (1934); *Chem. Abs.*, **28**, 7163 (1934).

[43] Bhagwat, W. V., and Dhar, N. R., *J. Indian Chem. Soc.*, **9**, 335 (1932); *Chem. Abs.*, **27**, 27 (1933).

[44] Allmand, A. J., *J. Chem. Soc.*, 1557 (1929).

[45] Style, D. W. G., "Photochemistry," p. 51, Methuen, London, 1930.

[46] Bhagwat, W. V., *J. Indian Chem. Soc.*, **11**, 443 (1934); *Chem. Abs.*, **28**, 7163 (1934).

Attempts to relate the rates of photochemical reactions to the dielectric constants of the solvents employed have not proved very profitable. Winther[47] found that, in the photoöxidation of iodoform and the polymerization of anthracene in a series of solvents, the velocity in general decreased with increasing dielectric constant of the solvent, but this could not be confirmed by Yajnik and Uppal.[48]

The earlier investigations are replete with instances of photochemical induction periods, or lags between the beginning of irradiation and start of reaction, and also of after-effects or a continuation of reaction after the close of the irradiation period. These effects are no longer regarded as of great general significance, the many known examples being considered merely as features of the mechanisms of the specific reactions in which they are encountered. At present, induction periods are usually regarded as the times required for the photochemical destruction of certain inhibitors present in small quantities.[49] Reactions claimed to exhibit after-effects have been reported by Mukerji and Dhar.[50] It must be noted that in chain reactions the reaction does not cease instantly when the illumination is cut off, as the secondary reactions continue for some time until all chains are broken. Similarly, when the intermediary in the chains is being formed and a stationary concentration (at which formation and destruction of the intermediary are equal) is being built up, the rate of the overall reaction (which depends upon the rate of destruction) need not attain its full value.

The influence of surface catalysts is of importance chiefly as they influence the recombination rate of free atoms or radicals. Coehn and Heymer[51] devised experiments in which hydrogen and chlorine were exposed to light without an opportunity of coming into contact with a solid surface. The formation of hydrogen chloride under these conditions proves that the reaction does not depend on an initial catalysis at a glass wall. Chapman and Grigg[52] have found the rate of this reaction to be less in capillary tubes than in wider ones. This is interpreted as meaning that the reaction is carried out (see Chapter 18) by means of an unstable catalyst (hydrogen and chlorine atoms) the latter being formed by light; these atoms are destroyed by recombination when they come in contact with glass.

Although irradiation of a graphite catalyst almost triples the rate at which it decomposes hydrogen peroxide, the effect is smaller for irradiated lead peroxide and still smaller or even non-existent in the case of smooth or slightly platinized platinum.[53] In the case of the decomposition at the surface of colloidal platinum, the velocity constant is the sum of those of the action of ultraviolet light and of the colloid separately on hydrogen peroxide.[54]

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[47] Winther, C., *Trans. Faraday Soc.*, 21, 595 (1926); see also Mathur, K. G., Gupta, R. S., and Bhatnagar, S. S., *Indian J. Physics*, 2, 243 (1927).

[48] Yajnik, N. A., and Uppal, H. L., *J. Indian Chem. Soc.*, **6**, 729 (1929); *Brit. Chem. Abs.* **A**, 174 (1930); *Chem. Abs.*, **24**, 1035 (1930).

[49] Earlier points of view are given by Purkayastha, R. M., *J. Indian Chem. Soc.*, **5**, 721 (1928); *Chem. Abs.*, **23**, 2105 (1929).

[50] Mukerji, B. K., and Dhar, N. R., *J. Indian Chem. Soc.*, **2**, 277 (1925); **5**, 203 (1928); *Chem. Abs.*, **23**, 41 (1929); *Quart. J. Indian Chem. Soc.*, **2**, 277 (1925); *Chem. Abs.*, **20**, 1953 (1926).

[51] Coehn, A., and Heymer, G., *Ber.*, **59B**, 1794 (1926).

[52] Chapman, D. L., and Grigg, P. P., *J. Chem. Soc.*, 3233 (1928).

[53] Pisarzhevskii, L. V., Korabel'nik, R. K., and Ruinskaya, E. S., *Bull. acad. sci. U.R.S.S., Classe sci. math. nat.*, 931 (1934); *Chem. Abs*, **29**, 2433 (1935).

PHOTOCHEMICAL EFFECTS OF INTERMITTENT AND POLYCHROMATIC LIGHT

The possibility of producing different effects by irradiating a system with a given quantity of intermittent or continuous light has been studied, notably by Padoa and Vita.[55] In some reactions, they claimed to secure greater reaction velocities by the use of intermittent light. The light was obtained by employing rotating sectors with a continuous source. In some instances the yield at first increased with the number of alternations of the sectors and then decreased to a constant value.[56]

Alternations of two or more colors with no periods of darkness caused a greater dependence of the yield on the velocity of alternation. Pulsating monochromatic light was also employed in some of their work.[57] The augmentation in yield depended both upon the wave-length of the light and the frequency of interruption, the maximum interruption being 560 times per second. In the oxidation of ferrous iodide by the 4607A line, the velocity was doubled by the use of intermittent light. This maximum rate was said to occur periodically as the frequency of interruption was increased, the maxima appearing irregularly at interruption frequencies of 32, 98, 138, 157, 202, 253, 270, 318, 357, 390, 450 and 513 per second. With green light, the yield ratio was lower (1.70), and the maxima fewer in number, occurring at 22, 259 and 532 interruptions per second. With yellow light the maximum ratio was 1.62 at 311 interruptions per second. Except at frequencies between 20, 40 and 260-370 interruptions per second, the yield was unaltered by intermittent illumination with this light. Red light gave a maximum yield ratio of 1.37 at 472 interruptions per second. The authors suggested that the periodic maxima might be due to the formation of active molecules which are the seats of adiabatic transformations, and that the life of these molecules is greater the greater their energy levels. Berthoud[58] was unable to confirm the existence of these maxima.

Berthoud and Bellenot[59] and Briers, Chapman and Walters[60] have used the rotating sector method in studying reactions whose rates are proportional to the square root of the light intensity, *e.g.*, the oxidation of potassium oxalate by iodine. The rate of the reaction varies as the concentration (in a steady state) of an intermediary, here assumed to be iodine atoms. The latter were formed at a rate proportional to the intensity of the light and destroyed at a rate proportional to the square of the concentration of the intermediary. The concentration of the catalyst in the steady state can therefore be shown to be proportional to the square root of the light intensity. When the sector rotates so rapidly that the secondary processes continue throughout the interval of darkness the rate is independent of the speed of rotation. When it rotates so slowly that the intermediary is exhausted by the secondary processes during each period of darkness, or is materially lowered in concentration during this period, the rate of the overall reaction will be lowered. By this method the life of the catalyst or intermediary has been calculated to be 0.03 to 0.12 second. Similar effects were observed by Briers and Chapman[61] in the case of the photosynthesis of hydrogen bromide, the mean life of the intermediary being 0.063 second.

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[54] Suirkin, Y., and Godnev, I. N., *J. Phys. Chem. (U.S S.R.)*, **5**, 32 (1934); *Chem. Abs.*, **28**, 4971 (1934). For other reactions in which surface effects have been held to play a part, see Kondrat'ev, V., *Z. Physik*, **48**, 310 (1928) and Kautsky, H., de Bruijn, H., Neuwirth, R., and Baumeister, W., *Ber.*, **66B**, 1588 (1933).

[55] Padoa, M., and Vita, N., *Gaz. chim. Ital.*, **57**, 187 (1927).

[56] Padoa, M., and Vita, N., *Atti II Congr. Naz. Chim Pura Applica.*, 1256 (1926).

[57] Padoa, M., and Vita, N., *Gaz. chim. ital.*, **58**, 461 (1928).

[58] Berthoud, A., *J. chim. phys.*, **26**, 444 (1929).

[59] Berthoud, A., and Bellenot, H., *Helv. Chim. Acta*, **7**, 307 (1924).

[60] Briers, F., Chapman, D. L., and Walters, E., *J. Chem. Soc.*, 562 (1926).

[61] Briers, F., and Chapman, D. L., *J. Chem. Soc.*, 1802 (1928).

Since truly monochromatic radiations are idealizations, all actual photochemical reactions are produced by the simultaneous action of more than one wave-length, even though these be but slightly different. Considerable work has been expended upon the effects produced by the simultaneous use of relatively widely separated wave-lengths. Plotnikow[62] claimed that the rate of bromination of cinnamic acid in carbon tetrachloride solution when simultaneously illuminated by several wave-lengths was less, in the ratio of 100 to 158, than the sum of the rates of the individual reactions when the wave-lengths were employed separately. Padoa and Vita[63] reported a confirmation of this behavior; they claimed also that the reaction rate does not decrease as the source is removed to greater distances to the extent demanded by the inverse square law. They reported a similar effect of complex light in diminishing the reaction rate of the decomposition of hydriodic acid, using 5460 and 5790A.[64] The opposite effect was reported in the case of the hydrogen-chlorine combination and in the action of light on direct-printing photographic paper, although in the latter case the order of the application of the wave-lengths used appeared to be a deciding factor.[65] Similar effects were also reported for the decomposition of ferric oxalate.

On the other hand, Berthoud,[66] who studied the oxidation of potassium nitrite by iodine in aqueous solution in yellow and blue light separately and together, found the effects to be purely additive. Winther[67] stated that the Italian workers neglected the induction periods of the reactions studied, employed incorrect methods of determining the rate of liberation of iodine in the hydrogen iodide decomposition, and employed erroneous transmission values for the filters.[68] It would appear that an interpretation of the Padoa experiments, assuming them to be correct, would imply that certain wave-lengths retard the effects produced by others. This raises the question as to whether any instances are known in which thermal reactions are retarded by light. Claims that such is the case were made by Chastaing[69] and by Trautz.[70] Details need not be given since re-examination of these reactions by Allmand and Maddison[71] failed to confirm the existence of the retarding effect; this has since been admitted by Trautz. With Haas, however, Trautz has recently[72] claimed that blue light accelerates and infrared retards the oxidation of benzaldehyde. It may be noted that it has frequently been suggested that the biological effects of ultraviolet rays may be annulled, at least in part by infrared rays.[73] However, others have proposed that the two forms of radiation should be applied simultaneously.[74] The Herschel effect in photography appears to be a case in which infrared radiations annul the effects of visible or ultraviolet radiations.

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[62] Plotnikow, J., *Z. physik. Chem* **79**, 641 (1912).

[63] Padoa, M., and Vita, N., *Gaz chim. Ital.*, **56**, 375 (1926); *Trans. Faraday Soc.*, **21**, 573 (1926).

[64] See also *Z. wiss. Phot.*, **28**, 153 (1930); Vita, N., *Gazz. chim. Ital.*, **63**, 223 (1933).

[65] Padoa, M., and Vita, N., *Gaz. chim. Ital.*, **56**, 164 (1926); *Chem. Abs.*, **20**, 2951 (1926); *Gaz. chim. ital.*, **58**, 3 (1928).

[66] Berthoud, A., *J. chim. phys.*, **26**, 435 (1929).

[67] Winther, C., *Z. wiss. Phot.*, **31**, 251 (1933); **33**, 52 (1934).

[68] See also for further details of the controversy *Z. wiss. Phot.*, **32**, 185 (1933).

[69] Chastaing, P., *Ann. Chim. Phys.*, **11**, 145 (1877).

[70] Trautz, M., *Physik. Z.*, **7**, 899 (1906); *Z. Elektrochem.*, **13**, 550 (1907).

[71] Allmand, A. J., and Maddison, R. E. W., *J. Chem. Soc.*, 650 (1927).

[72] Trautz, M., and Haas, H. E., *Z. wiss. Phot.*, **33**, 81, 129 (1934); *Chem. Abs*, **29**, 2869 (1935).

[73] Pech, J. L., *J. med. Bordeaux*, **10**, 434 (1925).

Plotnikow[75] has called attention to reactions which appear to proceed at periodic rates when illumination is furnished by complex light. He believes the concentration of free halogen in solutions of either bromine or chlorine in carbon tetrachloride to undergo periodic fluctuations when irradiated for prolonged periods with complex, but not with monochromatic, light.

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[74] Rowley, C. D., and Larsky, A. W., British P. 325,824 (1928).

[75] Plotnikow, J., *Z. Physik*, 32, 942 (1925).

Chapter 16

Photosensitized Processes

In photosensitized processes, the light which causes the reaction to proceed is absorbed, not by the reactants, but by some added substance which is capable of passing on the absorbed energy, or a sufficient portion of it, to the reactants. The simplest of such processes are those in which atoms act as photosensitizers.[1] Turner reviewed the earlier work on the excited systems formed when atoms absorb definite wave-lengths. Certain widely used terms regarding the nature of collisions in which excited atoms take part were introduced by Klein and Rosseland in 1921.[2] They called "collisions of the first kind" those in which a portion of the kinetic energy of two colliding atoms is expended in raising one of the atoms to an excited state. If, on the other hand, an excited atom loses a portion of its excitation energy during a collision, it is said to undergo a "collision of the second kind." It was demonstrated by Cario and Franck [3] that mercury atoms which had been excited by the absorption of radiations of the wave-length 2537A, a mercury resonance line, can undergo collisions of the second kind with thallium or sodium atoms. This means that during the collision the mercury atom passes some of its excitation energy to the atom with which it collides, raising the latter to an excited state. The excess of energy possessed by the excited mercury atom over that required to excite the thallium or sodium atom is converted into kinetic energy of the atoms separating after the collision. The excited alkali atom then, after a brief period, drops back to its normal state emitting the line corresponding to the energy lost in the transition from the excited state attained as the result of the collision. The effect observed experimentally is that, when a mixture of sodium and mercury vapors is irradiated with a monochromatic ray which is absorbed only by the mercury, the mixture emits a ray characteristic of sodium. Turner found that in processes of this kind, the excited mercury atom usually drops to the longer-lived metastable state before colliding with other atoms, at least under certain conditions of pressure.[4] Stuart's experiments [4a] on the quenching of the resonance fluorescence of mercury by radiationless collisions with foreign gas atoms indicated the excited mercury atom to have a larger effective radius that it has in the normal state.

The possibility that such collisions of the second kind of excited atoms with molecules might induce the molecules to enter reactions was soon recognized. Taylor, Marshall and Bates [5] found that hydrogen could be made to combine with oxygen when the gas mixture which had been bubbled through liquid mercury at the ordinary temperature, is irradiated with the resonance line of mercury obtained by the use of a cooled mercury arc. Such a reaction could not be induced by this line in the absence of mercury vapor.[6] At high rates of gas flow, hydrogen peroxide could be detected as a product of the reaction, and some mercuric oxide formed on the surface of the metal.[7] Taylor [8] reviewed the early work on this and many other gas reactions and claimed to have reduced carbon monoxide to formaldehyde, methane and polymerized hydrocarbons by this method. Similar work was reported by Hirst.[9] Taylor, Marshall and Bates [10] showed that the function of the mercury surface was merely to furnish mercury atoms, the reaction occurring in the vapor phase. Mercury atoms adsorbed on a copper catalyst [11] are usually not activated sufficiently in the light of a mercury arc to cause a reaction between hydrogen and ethylene.

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[1] Turner, L. A., *J. Phys. Chem*, **32**, 507 (1928). For a detailed discussion, see Mitchell, A. C. G., and Zemansky, M. W., "Resonance Radiation and Excited Atoms," Cambridge Univ. Press, 1934.

[2] Klein, O., and Rosseland, S., *Z. Physik,* **4**, 46 (1921).

[3] Cario, G., *Z. Physik,* **10**, 185 (1922); Cario, G., and Franck, J., *Ibid.,* **11**, 161 (1922); **17**, 202 (1923).

[4] See also Donat, K., *Z. Physik,* **29**, 345 (1925); Wood, R. W., *Proc. Roy. Soc. London,* **106A**, 679 (1924).

[4a] Stuart, H. A., *Z. Physik,* **32**, 262 (1925).

[5] Taylor, H. S., Marshall, A. L., and Bates, J. R., *Nature,* **117**, 267 (1926); see also Senftleben, H., and Rehren, I., *Z. Physik,* **37**, 529 (1926) for the discussion of water vapor.

In the mercury-sensitized, hydrogen-ethylene reaction, there are formed ethane, methane, propane and butane.[12] Three primary reactions are postulated:

(1) $H_2 + Hg^* \longrightarrow Hg + 2H$.
(2) A splitting off of hydrogen from ethylene.
(3) The opening of the ethylene double bond.

The last reaction is possible since it requires less energy than that corresponding to the 4.9 volts or 112 kcal. of excitation energy of the mercury atom. Bates and Taylor [13] extended the method to a wide variety of reactions, including many organic compounds. They found the excited mercury atom highly efficient in breaking the linkings, H—H, N—H and O—H. The decompositions obtained were often many hundreds of times those obtained by exposure of the reactants to the complete ultraviolet spectrum of the mercury arc without the addition of the sensitizer. From this it followed that the energies of these bonds must all be less than 112 kcal., a conclusion substantiated by thermal data. In the breakdown of ammonia, the percentage of hydrogen in the reaction products was found to be be greatly in excess of that required had a simple decomposition to the elements occurred. It was therefore, suggested that the reaction occurs in stages, in such a way that some nitrogen-rich substance such as hydrazine can be formed.[14] Mitchell [15] also reported on the fluorescence of ammonia excited by collisions with excited mercury atoms. Bates and Taylor [16] extended the investigation to sensitizations by cadmium vapor, but Bates found that cadmium atoms excited to the 2^3P_1 state did not possess sufficient energy to effect the reaction between hydrogen and ethylene.[17] The possibility of such a reaction can at present be determined directly from the energy-level diagram of the atom proposed as sensitizer and from the thermally known energy requirement for the reaction in question. In general, it has been found to be true that collisions of the second kind are most probable when the energy of the excited atom can be almost entirely consumed in the excitation of another atom or the disruption of a molecule. Processes in which there is much excess energy of excitation to be converted into kinetic energy are less probable.

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[6] Dickinson, R. G., *Proc. Nat. Acad Sci*, **10**, 409 (1924); Marshall, A. L., *J. Phys Chem*, **30**, 34, 1078 (1926).

[7] See also Bonhoeffer, K. F., and Loeb, S., *Z. physik. Chem.*, **119**, 474 (1926), and Hirst, H. S., and Rideal, E. K., *Nature*, **117**, 449 (1926).

[8] Taylor, H. S., *Trans. Faraday Soc.*, **21**, 560 (1926).

[9] Hirst, H. S., *Proc. Cambridge Phil. Soc.*, **23**, 162 (1926); *Chem. Abs.*, **20**, 2459 (1926).

[10] Taylor, H. S., Marshall, A. L., and Bates, J. R., *Nature*, **117**, 267 (1926).

[11] Ryerson, L. H., *Physics*, **2**, 70 (1932); for a recent summary, Norrish, R. G. W., *Trans. Faraday Soc.*, **35**, 21 (1939).

[12] Olson, A. R., and Meyers, C. H., *J. Am. Chem. Soc.*, **48**, 389 (1926); **49**, 3131 (1927).

[13] Bates, J. R., and Taylor, H. S., *Proc. Nat. Acad. Sci.*, **12**, 714 (1926); *J. Am. Chem. Soc.*, **49**, 2438 (1927).

[14] See also Dickinson, R. G., and Mitchell, A. C. G., *Proc. Nat. Acad. Sci.*, **12**, 692 (1926).

[15] Mitchell, A. G. G., *J. Am. Chem. Soc.*, **49**, 2699 (1927).

[16] Bates, J. R., and Taylor, H. S., *J. Am. Chem. Soc.*, **50**, 771 (1928).

[17] Bates, J. R., *Proc. Nat. Acad. Sci.*, **14**, 849 (1928).

Apparatus for effecting gas reactions photosensitized by metal vapors has been patented.[18] Among the reactions for which it was intended was the conversion of water gas into formaldehyde.[19]

It is a comparatively simple step from the consideration of these reactions to that of those in which the sensitizer is a molecule rather than an atom. Dhar and Mukerji[20] and also Berthoud[21] discussed the use of chlorine as a sensitizer for the decomposition of ozone, and Taylor and Emeléus[22] considered photosensitization by means of ammonia. In such cases, one is dealing with dissociated and not excited molecules. The dissociation products can initiate chain reactions. Details of these processes will be considered in later chapters in dealing with individual reactions.

Other Theories of Photosensitization.[23] Many instances of photosensitization by solids, as zinc oxide, have been described. Colloidal hydrous stannic oxide or ignited stannic oxide is said to enable sunlight to effect the oxidation of ammonia to nitrite or the reduction of nitrates to nitrites, and also to decolorize such dyes as methyl violet, methylene blue or brilliant green. The yields are very small.[24]

Irradiation of a crystal of cadmium sulfide so alters the potential of its surface field as to lessen its ability to adsorb phenolphthalein from an alcoholic solution.[25]

A novel theory of sensitized photolysis, developed by Baur[26] to explain the action of zinc oxide or uranyl salts in promoting various photochemical processes, has also been extended to cover certain cases of sensitization by dyes. The sensitizer is thought to become on absorption of light a polarized molecule, comparable to the two electrodes of an electrolytic cell.[27] In the case of uranyl salts, the absorption process is written:

$$5\mathrm{U}^{\mathrm{VI}} + h\nu \longrightarrow \left\{ \begin{array}{l} 3\mathrm{U}^{\mathrm{VIII}} \\ 2\mathrm{U}^{\mathrm{III}} \end{array} \right.$$

In a more general form, it may be written:

$$\mathrm{U}^{\mathrm{VI}} + h\nu \longrightarrow \mathrm{U}^{\mathrm{VI}} \left\{ \begin{array}{l} \oplus\oplus \\ \ominus\ominus \end{array} \right.$$

The displaced electrons return to their original state through a "molecular electrolysis," the energy for which is derived from the increase in the potential energy of the valence electrons attained during the process of light absorption. The positive and negative poles in the molecule act as anode and cathode in a kind of molecular electrolysis. Using silver nitrate as cathodic depolarizer and sucrose, glycine or glycerol as anodic depolarizer, the sensitizing action of the following dyes has been studied: rhodamine B, eosin, safranine-G, phenosafranine, fluorescein, methyl violet, chromotrope-2R. The photolysis results in the separation of silver and the concomitant formation of oxidation products. Some silver was liberated in the binary systems, silver nitrate-dye, silver nitrate-sucrose, but a larger amount was set free in the ternary systems composed of dye and depolarizers.

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[18] I. G. Farbenindustrie A.-G., British P. 307,406, Feb. 11, 1927; 307,521, Feb. 11, 1927; *Chem. Abs.*, **23**, 5112 (1929).

[19] See also Frankenburger, W., and Steigerwald, C., German P. 513,461, Nov. 21, 1926; *Chem. Abs.*, **25**, 1303 (1931); Frankenburger, W., and Mayrhofer, K., German P. 528,040, Sept. 4, 1927 (to I. G. Farbenindustrie); Buttolph, L. J., U. S. P. 1,844,421, Feb. 9, 1932 (to General Electric Vapor Lamp Co.).

[20] Dhar, N. R., and Mukerji, B. K., *Trans. Faraday Soc.*, **21**, 645 (1926).

[21] Berthoud, A., *Trans. Faraday Soc.*, **21**, 554 (1926).

[22] Taylor, H. S., and Emeléus, H. J., *J. Am. Chem. Soc.*, **52**, 2150 (1930).

[23] Work on photosensitization has been reviewed by Farkas, L., Haber, F., and Harteck, P., *Z. Elektrochem.*, **36**, 711 (1930) and by Livingston, R., *J. Chem. Ed.*, **11**, 400 (1934).

[24] Varadanam, C. I., and Rao, G. G., *Current Sci.*, **7**, 231 (1938); *Chem. Abs.*, **33**, 1598 (1939).

[25] Hedvall, J. A., and Gohn, G., *Nature*, **143**, 330 (1939); note also Vartanyan, A. T., *J. Gen. Chem. (U.S.S.R.)*, **8**, 1098 (1938); *Chem. Abs.*, **33**, 4878 (1939).

[26] Baur, E., *Helv. Chim. Acta*, **1**, 186 (1918); **12**, 793 (1929); *Z. Elektrochem.*, **34**, 595 (1928).

[27] Burgher, K., *Z. wiss. Phot.*, **24**, 393 (1927). Baur has attempted to use his concept in explaining the assimilation of carbon dioxide by plants, *Helv. Chim. Acta*, **20**, 387 (1937).

The sensitized photolysis very soon reaches a stationary state, apparently owing to the formation of a new anodic depolarizer which begins to compete with the existing depolarizer. The experiments with glycine and glycerol show that these substances can be further oxidized in this manner.

The investigation of Burgher lends support to an inner polarization mechanism for sensitization. It may also be noted that in certain instances photosensitization may be ascribed to the absorption of light by complexes formed between the sensitizer and one of the reactants, neither of the components absorbing alone. Instances will be discussed in the treatment of specific reactions.

The ability of a series of complex cobalt salts to sensitize the oxidation of potassium iodide, pyrogallol, benzidine, *p*-phenylenediamine and other substances when both the substrate and sensitizer are irradiated, usually by the 3660A line, was studied by Watanabe.[28] Of the nitro-cobaltic compounds, those which had two nitro-groups attached to the nucleus were most strongly affected by light. The oxidizing ability of the croceo-chloride (*trans*) was more photosensitive than that of the flavo-chloride (*cis*), which showed oxidizing action even in darkness. The magnitude of the photoactivity of nuclei of the type $Co(NH_3)_5X$ was influenced by the coordinated acid radical in the order $SCN > NO_2 > CO_3 > Cl$.

Mukerji and Dhar[29] find that in photosensitized systems there is a marked increase in the light absorption not found in systems they believe to be photoinhibited. Dhar and Bhattacharya[30] suggest that the presence of a second reactant may sensitize molecules to radiation of longer wave-length.

Relation of Fluorescence to Sensitization.[31] An understanding of the nature of the photodynamic action of many fluorescent dyes upon living organisms (Chapter 42) and of the function of chlorophyll in the photosynthesis of carbohydrates (Chapter 43) depends upon the advances in our knowledge of the mechanism of photosensitization by these fluorescent substances. A much discussed recent question is whether the reactions effected by these agents are to be ascribed to their fluorescence or whether this property is merely an incidental phenomenon which may even lessen their effectiveness as sensitizers. Viale[32] believed that, since the additions of foreign substances to dyes lessened both their fluorescence and their effectiveness as sensitizers, the fluorescence was in some manner responsible for their sensitizing action. West, Müller and Jette,[33] however, pointed out that any addition of ions in solution which tends to destroy an activated molecule will simultaneously destroy the ability of that molecule to impart its energy to a chemical reaction or to emit it as fluorescence. The addition of reactants, which

[28] Watanabe, A., *Iwata Inst. Plant Biochem. Publ.*, 2, 129 (1936); *Chem. Abs.*, **30**, 6650 (1936).

[29] Mukerji, B. K., and Dhar, N. R., *J. Indian Chem. Soc.*, **5**, 411 (1928); *Chem. Abs.*, **23**, 40 (1929).

[30] Dhar, N. R., and Bhattacharya, A. K., *J. Indian Chem. Soc.*, **11**, 33 (1934); *Brit. Chem. Abs.*, **1934A**, 496.

[31] For earlier theoretical discussions, see Steigmann, A., *Kolloid-Z.*, **44**, 173, 248 (1928); *Z. wiss Phot.*, **26**, 299 (1929).

[32] Viale, G., *Arch. ital. biol.*, **73**, 19 (1924); *Chem. Abs.*, **19**, 2346 (1925).

[33] West, W., Müller, R. H., and Jette, E., *Proc. Roy. Soc. London*, **121A**, **294**, 299, 313 (1928).

may remove excitation energy by collisions of the second kind and thus render it available to the reaction, also decreases the fluorescence. Many believe that the primary process in the reactions underlying photodynamic oxidations by dyes is the quenching of their fluorescence in solution by reactants.[34] Others, however, believe that, in general, photosensitized reactions in solution proceed rather by the use of energy absorbed in linkings or parts of the sensitizing molecule which never appears as fluorescence.[35]

The mechanism of the fluorescence of dyes and of its quenching has been the subject of much recent work. The advances in this, possibly the phase of photochemistry at present the most rapidly developing, have been summarized in a recent discussion of the Faraday Society.[36] Although the subject is still in a somewhat confused state, certain concepts have emerged.

Pringsheim[37] points out that fluorescence is the exception rather than the rule in organic molecules, most substances with large light absorption converting the energy thus acquired into heat by little understood mechanisms. He finds little known regarding the conditions that must be met in order that a substance in a condensed phase may fluoresce. One view is that, since the absorption of fluorescent dyes lies in the visible region, the quanta gained by absorption are too small to initiate quenching processes and, therefore, can only be lost by fluorescence. This seems inadequate since a large number of dyes with visible absorption are not fluorescent. In the rare earths and uranyl compounds, the narrowness of the absorption bands has been held to indicate that the electron transfer process is well protected against fluorescence. Although this seems true also of chloropyhll and porphyrins, it does not apply to many dyes, such as uranin or trypaflavin, so that it is improbable that there can be a definite correlation between the fluorescence of a compound and the width of its absorption bands. Furthermore, there seems to be no parallelism between the electrical conductivity of a dye and its fluorescence, although it is true that, as in the case of fluorescent indicators, the absorption spectra and fluorescence may vary with the state of ionization of the dye. Weiss[36] believes that all organic molecules with strong fluorescence have conjugated band systems in which the excitation energy is not easily transformed into heat, or in other words, that there is no coupling between free electrons of these systems and the vibrations of the heavy particles. Mumm[38] regards the fluorescent substance as an intermediate state (resonance form) between two end structures. Absorption raises an electron to an excited state from which it drops to one of the end states with the appearance of fluorescence. This end structure then passes to the intermediate state with evolution of heat. He has applied this theory, developed for N-methyl-α-pyridones, to the fluorescence of barium platinocyanide and to uranyl salts.

A number of studies have been concerned with the measurement of the fluorescence efficiency of dyes and other substances. Some materials, as solid anthracene, have high efficiencies approximating unity. In various solvents, however, anthracene has maximal efficiencies which vary from 0.28 to 0.01. Bowen and Norton[39] find that the fluorescence efficiency F depends on the nature of the fluorescent substance, the solvent, concentration of solute, temperature and concentration c of quencher. It may be expressed by $F = \frac{k_1}{1 + k_2C}$ in which k_1 and k_2 are constants. Many processes tend to lower the efficiency in solution. Some, such as an inner filtering action of some solute or of the solvent, or the formation of non-fluorescent compounds with the solvent, or the formation of aggregates,[40] do not appear to be related to true quenching processes. The progressive introduction of halogens into such a dye as fluorescein diminishes the fluorescence; for this the somewhat misleading term "internal quenching" has been suggested.

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[34] Noack, K., *Naturwiss.*, **14**, 383 (1926); *Chem. Abs.*, **20**, 2521 (1926); **21**, 2011 (1927); *Biochem. Z.*, **183**, 144 (1927); Gaffron, H., *Biochem. Z.*, **179**, 157 (1926).

[35] Shpol'skiĭ, E., and Sheremet'ev, G., *J. Phys. Chem. (U.S.S.R.)*, **8**, 640 (1936); *Chem. Abs.*, **31**, 2100 (1937).

[36] *Trans. Faraday Soc.*, **35**, 15 (1939).

[37] Pringsheim, P., *Ibid.*, **35**, 28 (1939).

[38] Mumm, O., *Ber.*, **72B**, 29 (1939). For an earlier discussion of theories of fluorescence, see Perrin, F., *Ann. Physique*, **12**, 169 (1929).

[39] Bowen, E. J., and Norton, A., *Trans. Faraday Soc.*, **35**, 44 (1939).

True quenching of fluorescence in solution refers to a process in which the excitation energy absorbed by a certain percentage of the absorbing molecules may be transferred to other molecules before it can be emitted as light.[41] Two types have been distinguished. The quenching is said to be static when the quenching molecule is within the sphere of action of the fluorescent molecule during the absorption process. When the quencher must diffuse toward the excited molecule during its lifetime, the quenching is said to be diffusional. Many strong quenchers of dye fluorescence act in this manner.

The quencher may be an inorganic ion, as studied by West, Müller and Jette,[42] a foreign molecule as oxygen, or even other molecules of the fluorescent substance. If the latter, the process of quenching (self-extinction) generally causes the fluorescence intensity to decrease with an increasing concentration of the dye. Self-extinction may be regarded as due to collisions of the second kind between like molecules. Kautsky,[43] however, claims that this is incorrect and that self-extinction is due to a lengthening of the life of the excited molecules. This view is based chiefly upon observations of fluorescent solids which show increased phosphorescence with decreased fluorescence. Kautsky claims that in liquids long-lived states may be produced, although the phosphorescence lasts but 10^{-8} sec. because of the greater ease of the conversion of excitation energy into thermal energy. Concentration quenching occurs at such low concentrations as 10^{-4} mole per liter in the case of anthracene solutions. Pringsheim points out that this could scarcely be accounted for by energy resonance between excited and unexcited molecules. He suggests that it may more likely be related to a utilization of part of the energy in some photochemical change, the excess being converted into heat. In the case of anthracene, the reaction is the formation of dianthracene (Chapter 26). The self-extinction of fluorescence is also encountered in the case of the photochemical reactions of other hydrocarbons with condensed ring systems.

Other molecules, *e.g.*, non-fluorescent dyes, with absorption bands overlapping those of the fluorescent substance, act as strong quenchers. Many antioxidants,[44] phenols, amines and the iodide ion act as quenchers. In such cases, little is known of the mechanism of quenching. Most quenchers act only after many collisions and in some cases it is believed that the quenching is stepwise. Since the temperature has little influence, no activation seems necessary.

In the Faraday Society discussion, D. D. Eley suggested that the magnetic effect of such paramagnetic ions as Fe^{++}, Ni^{++}, Cu^{++} may quench the fluorescence of porphyrins by a magnetic predissociation process. Halide ions might also quench dyes by a predissociation process induced by their electric fields did their hydration envelopes not prevent the ions from approaching closely enough. Weiss, however, showed that strong magnetic fields do not affect the fluorescence of dye solutions, and believed the halide ions to act by a radiationless transfer of an electron from the ion to the excited dye. This theory may be compared with the view of Hachkowskiĭ and Terenin[45] that molecules adsorbed on fluorescent solids quench by taking up free electrons from the solids to form negative ions.

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[40] Kortüm, G., *Z. physik. Chem.*, **33B**, 1 (1936); **34B**, 255 (1936); Lewschin, W. L., *Acta Physicochim. U.S.S.R.*, **2**, 221 (1935); *Chem. Abs.*, **29**, 7798 (1935).

[41] Franck, J. M., and Wawilow, S J., *Z. Physik.*, **69**, 100 (1931); Sveshnikov, B., *Acta Physicochim. U.R.S.S.*, **3**, 257 (1935); **4**, 453 (1936); **7**, 755 (1937); *Chem. Abs.*, **30**, 3327 (1936); **31**, 5681 (1937); **32**, 4880 (1938).

[42] West, W., Müller, R. H., and Jette, E., *Proc. Roy. Soc. London*, **121A**, 294, 299, 313 (1928).

[43] Kautsky, H., and Merkel, H., *Naturwiss.*, **27**, 195 (1939).

[44] Perrin, J., *Compt. rend.*, **184**, 1097 (1927); Privault, *Ibid.*, **184**, 1120 (1927).

Weiss[46] has developed his theory in considerable detail and employed it to interpret a number of experimental observations. The irradiation with a 1500-watt carbon arc of a methylene blue solution in the presence of the ferrous ion, causes a bleaching which is reversed when the irradiation ceases.

$$\mathrm{M\,B} + 2\mathrm{Fe}^{++} + 2\mathrm{H}^{+} \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} \underbrace{\mathrm{M\,B,H_2}}_{\text{leuco-dye.}} + 2\mathrm{Fe}^{+++}$$

Although the iodide ion had no similar effect on methylene blue, it did cause a bleaching action, proportional to the square root of the light intensity, on Lauth's violet and a slight one on eosin. Weiss holds that when an excited dye molecule D^* collides with an acceptor molecule or ion which has an electron in a level corresponding to that left vacant by the electronic shift in the dye excitation, the electron passes to the excited dye, forming the non-fluorescent excited D^-.

$$\begin{aligned} &D^* + \text{Accep.} \rightleftharpoons D^- + \text{Accept}^+ \\ &D^* + I^- \rightleftharpoons D^- + I \\ &D^* + Fe^{++} \rightleftharpoons D^- + Fe^{+++} \end{aligned}$$

A quantum mechanical resonance between the states (D^*, Accep) and D^-, Accep^+) is assumed. The dye molecule with the electron thus acquired may then on combination with a proton form a semiquinone DH, two molecules of which react to form the leucobase and oxidized dye.

$$\begin{aligned} &D^- + H^+ \longrightarrow DH \\ &2DH \longrightarrow DH_2 + D. \end{aligned}$$

It was possible to develop mathematical relations between the relative effectiveness of various halogen ions in quenching dye fluorescence and their electron affinities.[47]

The reactions described may also be used to explain the dye-photosensitized oxidation of larger quantities of ferrous ion, iodide ion or other acceptor, since when the semiquinone or leucobase has been formed, it can be reoxidized thermally to the dye by the air and thus be made capable of oxidizing more of the acceptor.

It will be noted that this theory takes no account of any effect which oxygen itself may have upon the fluorescence of the dye.[48] It has, however, been demonstrated that the fluorescence of chlorophyll or hematoporphyrin can be quenched by molecular oxygen, and cannot be quenched by acceptors, such as thiosinamine or isoamylamine. Such observations led Kautsky[49] to propose a different theory of photosensitized oxidations according to which it is assumed that collision with an excited dye molecule raises an oxygen molecule into a metastable excited state. Gaffron[50] disagreed with this (for further details see Chapter 44) and Franck and Levi[51] suggested that the HO_2 molecule may be formed in the quenching process and subsequently react with an acceptor. Weiss suggests the possibility of the O_2^- ion instead, believing its formation especially likely in the case of the collision of an oxygen molecule with an absorbed and excited dye such as trypaflavine.[52]

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[45] Hachkowskiĭ, V., and Terenin, A., *Acta Physicochim. U.R.S.S.*, **7**, 521 (1937).

[46] Weiss, J., *Trans. Faraday Soc.*, **32**, 1331 (1937); **35**, 48 (1939); *Nature*, **135**, 648 (1934); **136**, 794 (1935); Weiss, J., and Fishgold, H., *Z. physik. Chem.*, **32B**, 135 (1936); *Nature*, **137**, 71 (1936).

[47] See also Weber, K., *Z. physik. Chem.*, **30B**, 69 (1935).

[48] Schneider, E., *Z. physik. Chem.*, **28B**, 311 (1935).

In his most recent work, Kautsky[53] studies particularly the phosphorescence of dyestuffs adsorbed on silica or alumina gels and maintained in an evacuated vessel. The phosphorescence is said to be quenched by oxygen independently of its pressure down to a few thousandths of a mm. The quenching of the fluorescence, however, is said to depend upon the oxygen pressure. Kautsky interprets these experiments as favoring the formation of metastable oxygen molecules, since he could detect their diffusion by the following method. A mixture of fine grains of silica gel with adsorbed sensitizer and larger grains of silica gel with adsorbed leuco-methylene blue became blue when the oxygen pressure was made just small enough to quench the fluorescence of the sensitizer. When both the sensitizer and the acceptor are adsorbed on the same surface, the diffusion path is shortened and in light the color becomes blue at pressures up to one atmosphere. Such a mixed adsorbate is regarded as representing a transition to the conditions encountered in solution. An essential feature of Kautsky's theory is the phosphorescence, some oxygen-free solutions of sensitizers being reported to exhibit light for as long as 10^{-2} sec., after illumination, whereas the life of the usual excited state which causes fluorescence is only of the order of 10^{-8} sec. This phosphorescence, the yield of which is small, is thought to occur only in regions where there is slight association of the dye molecules. This afterglow is thought to be due to metastable excited states of dyes capable of causing but weak fluorescence. The afterglow can be demonstrated by the addition to 20 cc. of acetone of two to four drops of a 0.006 molar solution of any such efficient photosensitizers of oxidation as isoquinoline red, benzoflavine, eosin, hematoporphyrin, chlorophyll, erythrosin, phloxin or rose Bengal.[54] Strongly fluorescent compounds do not exhibit it under these conditions. A very small concentration of oxygen inhibits the afterglow, but the oxygen acceptors, thiosinamine and isoamylamine, have no effect.

Scheibe[55] suggests that in solution certain dyes may occur as polymers of several hundred molecules. The polymer may absorb many quanta simultaneously. This energy may be lost by fluorescence or by collision with a foreign molecule which may thus acquire a very large number of quanta, resulting in the formation of short-lived intermediate products at energy levels which could never be attained by the direct absorption of light.

Claims of the existence of a negative photosensitization have been made. Milbauer[56] observed that in the presence of 0.02, 0.2 or 1.0 mg. of the dyes Nile blue, Brilliant Green, Capri Blue, phenosafranine, fuchsin, pinacryptol green or methylene violet per 10 cc., the rate of decomposition of an active methanol solution containing 28.2 gm. per liter of sodium N-chloro-*p*-toluenesulfonamide is slower than in their absence, when exposed to intense visible light. Since simultaneous experiments with these dye mixtures in darkness did not show a loss of activated chlorine, it was believed that a negative photocatalysis had been demonstrated. In the same range of concentrations, malachite green, pinacryptol yellow and methylene blue did not exhibit this phenomenon, for in darkness they consumed activated chlorine and were themselves decomposed.

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[49] Kautsky, H., and de Bruijn, H., *Naturwiss.*, **19**, 1043 (1931); Kautsky, H , *Ber.*, **65**, 1762 (1932); *Trans. Faraday Soc.*, **35**, 216 (1939).

[50] Gaffron, H., *Biochem. Z.*, **264**, 251 (1933); *Ber.*, **68**, 1409 (1935).

[51] Franck, J., and Levi, H., *Naturwiss.*, **23**, 229 (1935).

[52] See Pringsheim, P., and Vogels, H., *J. chim. phys.*, **33**, 345 (1936).

[53] Kautsky, H., *Trans. Faraday Soc.*, **35**, 216 (1939).

[54] Kautsky, H., Hirsch, A., and Flesch, W., *Ber.*, **68B**, 152 (1935).

[55] Scheibe, G., *Naturwiss.*, **25**, 795 (1937).

[56] Milbauer, J., *Chem. Listy*, **29**, 267 (1935); *Phot. Korr.*, **71**, 94; *Chem. Abs.*, **30**, 1661 (1936).

A more complete discussion of the phenomena of luminescence and phosphorescence lies beyond the scope of this book, although in some instances ultraviolet radiations may be employed in eliciting these phenomena. Some developments of the earlier work in these fields led to significant work on the nature of the coloration produced in alkali halide crystals by irradiation. These are discussed in Chapter 21. A general discussion of the mechanism of phosphorescence has been given by Pohl.[57] A phosphor may be defined as an insulating crystalline material into which a minute trace of a highly refracting substance has been incorporated in the molten state. Excitation consists in the liberation of electron by photoelectric effects; luminosity arises from the return of such electrons to the normal state.

Chemoluminescence. This phenomenon represents, in a way, the converse of a photochemical change or of a photosensitized reaction. It is a process in which light is evolved during the course of a chemical reaction; the efficiency is seldom more than 1 per cent. Limitations of space prevent the discussion of this topic. For recent discussions, see Kautsky,[58] Nichols,[59] Beutler,[60] and a report of the National Research Council.[61]

PHOTOCHEMICAL REACTIONS IN SURFACES

Recently an attempt has been made to develop the theory that the velocity of photochemical reactions conducted in mono- or multi-molecular layers at the surface of a liquid depends upon the molecular orientation of the absorbing molecules.[62] Among the reactions studied have been the hydrolysis of stearic anilide spread on half-normal sulfuric acid, the decomposition of α-hydroxystearic acid with liberation of carbon dioxide produced by wave-lengths shorter than 2480A, the oxidation and hydrolysis of proteins, etc. The effects of traces of such sensitizers as nickel and copper and of inhibitors as potassium cyanide is, in some cases, pronounced.

On glass of refractive index 1.5, invisible multilayers of barium acid stearate (containing equal parts of stearic acid and barium stearate in each) when irradiated by a high-pressure mercury arc showed interference colors. Five minutes of irradiation of a 48-layer film caused a loss of optical thickness which amounted to one layer.[63] The loss continued for several hours after the irradiation had been stopped, finally amounting to more than two layers. A similar change occurs in pure stearic acid layers, but barium stearate shows only one twentieth this loss.

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[57] Pohl, R. W., *Naturwiss.*, **16**, 477 (1928), see also Melville, H. W., *Science Progress*, **33**, 527 (1939); Leverenz, H. W., and Seitz, F., *J. Applied Physics*, **10**, 479 (1939); Symposium on Luminescence, *Trans. Faraday Soc.*, **35**, 2 (1939).

[58] Kautsky, H., *Trans. Faraday Soc.*, **21**, 591 (1925).

[59] Nichols, E. L., *J. Opt. Soc. Am.*, **20**, 106 (1930).

[60] Beutler, H., *Angew. Chem.*, **45**, 249 (1932); Beutler, H., and Polanyi, M., *Z. Physik*, **47**, 379 (1928).

[61] *Bull. Nat. Research Council*, **59**, 30 (1927).

[62] Mitchell, J. S., *J. Chem. Physics*, **4**, 725 (1936); **5**, 83 (1937); Mitchell, J. S., Rideal, F. K., and Schulman, J. H., *Nature*, **139**, 625 (1937); Rideal, E. K., and Mitchell, J. S., *Proc. Roy. Soc. London*, **159A**, 206 (1937).

[63] Schaefer, V. J., *Science*, **89**, 465 (1939).

It is believed that radiations of 2300-2700A split the molecules of stearic acid at the attachment of the carboxyl group.

PHOTOCHEMISTRY AND OPTICAL ACTIVITY

There have been many attempts to prepare optically active substances by methods such that the form with one configuration results in larger amount than its antipode. One of the first successful experiments was performed in 1930 by Kuhn and Knopf.[64] It involved the use of circularly polarized light in causing the decomposition of α-azidopropiondimethylamide. This compound has an absorption band at about 2900A with a strong anisotropic factor of 0.02-0.03.[65] When acted upon in hexane solution by circularly polarized light of this wave-length, it undergoes decomposition of the azido-group, one stereoisomer being decomposed to a greater extent than the other. This is because the difference between the absorption coefficients of the compound for right and left circularly polarized light is, as stated, about 2 to 3 per cent. From the amount of nitrogen liberated, it was shown that the reaction follows approximately the Einstein equivalence law. The unchanged dimethylamide can be separated from the reaction products by distillation. When 40 per cent of the original racemic compound had been decomposed, the remainder showed in a 10-cm. polariscope tube a rotation of +0.78° when the irradiation had been conducted with *d*-circularly polarized light and of −1.04° when *l*-circularly polarized light had been used. The order of magnitude of these effects was in agreement with theoretical predictions. Kuhn, with Braun [66] had made earlier similar observations on ethyl α-bromopropionate in which near ultraviolet bands powerfully influence the optical activity.

Important earlier contributions to the field of asymmetric synthesis employing circularly polarized light and magnetic fields were made by Cotton.[67] In these experiments, active molecules were not, however, produced, as there resulted only an active arrangement of the molecules in a medium.[68] Studies of the photodichroism and photoanisotropy of light-sensitive solid layers of a gelatin photographic emulsion have been made by Weigert.[69] The primary action in induced photodichroism is assumed to be the deformation of micelles held together by van der Waals forces. The form of the spheres detached within the micelles depends on the waveform of the exciting light.[70]

There have been other recent attempts to obtain a total asymmetric synthesis. Davis and Haggie [71] reported the production of optically active trinitrostilbene dibromide by the photobromination of 2,4,6-trinitrostilbene by circularly polarized light of wave-lengths 3600 to 4500A. As solvents, they used carbon tetrachloride, benzene, glacial acetic acid and nitrobenzene. The last was the most suitable. In every case the reaction mixture assumed an optical activity which increased to a maximum and then decreased slowly and finally disappeared as the reaction proceeded to completion. Since the product on standing, whether in ordinary or in polarized light, loses its optical activity and since this cannot be restored by further exposure to polarized light, it was inferred that optical activity arises at the moment of the synthesis of the compound. The degree of rotation secured, although small (0.04°), was beyond the limit of error of the observations. The reaction is a chain, initiated by excited bromine atoms in which activated trinitrostilbene molecules may or may not take part. In diffused daylight or in unpolarized light, the reaction failed to form optically active material. Optically inactive trinitrostilbene dibromide is not rendered active by exposure of its solutions in nitrobenzene to circularly polarized light. In these experiments, the circularly polarized light was obtained by reflecting the light of a glass-enclosed mercury arc filtered through blue cobalt glass at the polarizing angle from a plate of black glass and by passage through a thin sheet of mica. No optically active product could be obtained by the use of circularly polarized light of wave-length 5890-5896A. The formation of optically active material was also observed when chlorine reacted with trinitrostilbene in nitrobenzene solution in circularly polarized light of wave-lengths between 3600 and 4500A. The reaction was much faster than in the case of bromine but no greater activity could be obtained. Maximum rotations were obtained in about 45 minutes.

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[64] Kuhn, W., and Knopf, E., *Naturwiss.*, **18**, 183 (1930); *Z. physik. Chem.*, **7B**, 292 (1930); *Ber.*, **63B**, 190 (1930).

[65] The theory of the relation between circular dichroism and optical rotatory power within and without absorption bands previously developed by Kuhn, W., *Z. physik. Chem.*, **4B**, 14 (1929) led to this work.

[66] Kuhn, W., and Braun, E., *Naturwiss.*, **17**, 227 (1929).

[67] Cotton, A., *Compt. rend.*, **189**, 657 (1929).

[68] See also Zocher, H., and Koper, K., *Z. physik. Chem.*, **132**, 295, 302, 313 (1928); Bruhat, G., *Bull. soc. chim.*, **47**, 251 (1930).

[69] Weigert, F., *Z. physik. Chem.*, **3B**, 377, 389 (1929); **4B**, 83 (1929). See also Chapter 21.

[70] Weigert, F., *Z. physik. Chem.*, **10B**, 241 (1930); Ghosh, J. C., *J. Indian Chem. Soc.*, **16**, 51 (1939); *Chem. Abs.*, **33**, 5744 (1939).

[71] Davis, T. L., and Haggie, R., *J. Am. Chem. Soc.*, **57**, 377 (1935).

Attempts of this sort had been previously made by Ghosh and Purkayastha [72] in the bromination of stilbene and of cinnamic acid, but the formation of optically active materials was not described. They found for the same intensities, ordinary light and plane polarized light to be equally effective, and circularly polarized light slightly less so. In the decomposition of potassium manganioxalate, however, it was slightly more effective than either non-polarized or plane-polarized light.[73]

By irradiating methyl (4-methylphenyl)(*p*-ethylphenyl)trimethylmethane with circularly polarized light of 4300A while introducing chlorine at 0°, Karagunis and Drikes [74] claimed to have obtained an optical rotation of 0.1° When light (5890A) which lies within the absorption band was used, the opposite rotation appeared.

Observations by Baly and Semmens [75] regarding the action of plane polarized light in hydrolyzing starch in plant leaves stimulated a large amount of work in which it was attempted to show that polarized light is more effective than ordinary light in effecting various photochemical reactions. Whatever may subsequently be found in regard to the action of plane polarized light upon substrates the molecules of which are definitely oriented in surface layers, in solids or in biological structures, there is no reason to expect it to be more effective than ordinary light of equal intensity in effecting photochemical reactions in solutions in which the substrate molecules have a random orientation. It has been shown by Bhatnagar, Anand and Gupta [76] that no differences are to be observed in the photochemical reactions by polarized and ordinary light between diammonium oxalate and mercuric chloride or in the decomposition of alkaline hydrogen peroxide.

Nevertheless, it has been claimed [77] that polarized light produces changes in the pharmacological properties of a number of drugs not produced by irradiation with non-polarized light. Irradiation of tincture of digitalis with polarized light was said to produce a deterioration as shown by a weakened pharmacological action. When ultraviolet light is used a further change or decomposition occurs and the tincture becomes more poisonous. With digitalis, it was claimed that circularly polarized light produced even greater deterioration than did plane polarized light. Macht and Krantz [78] stated that in these experiments the test and control solutions were simultaneously irradiated with polarized and non-polarized light of equal intensity.

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[72] Ghosh, J. C., and Purkayastha, R. M., *Quart. J. Indian Chem. Soc.*, **2**, 261 (1925); *Chem. Abs.*, **20**, 1953 (1926).

[73] Ghosh, J. C., and Kappanna, A. N., *Quart. J. Indian Chem. Soc.*, **3**, 127 (1926); *Chem. Abs.*, **20**, 3646 (1926).

[74] Karagunis, G., and Drikes, O , *Naturwiss.*, **21**, 607 (1933); *Chem. Abs.*, **28**, 144 (1934).

[75] Baly, E. C. C., and Semmens, E. S., *Proc. Roy. Soc. London*, **97B**, 250 (1924).

[76] Bhatnagar, S. S., Anand, H. L., and Gupta, A. W., *J. Indian Chem. Soc.*, **5**, 49 (1928); *Chem. Abs.*, **22**, 3840 (1928). Zhalkovskii, B. G., *Bull. biol. med. exptl. U R.S.S.*, **5**, 493 (1938); *Chem. Abs.*, **33**, 2544 (1939). See also Bhatnagar, S. S., Lal, R. B., and Mathur, K., *Nature*, **118**, 11 (1926) for physiological effects claimed to be due to polarized light.

On the other hand, Dailey and Benedict [79] were unable to show that polarized light had any selective action in the decomposition of cocaine hydrochloride, when irradiation times of from one to twelve hours were employed. This is at present generally believed to be true of photochemical reactions of substances under conditions in which they are capable of free and random orientation. Other workers to deny the claims for a special effectiveness of polarized light have been Bunker and Anderson [80] and Bond and Gray.[81]

PHOTOTROPY

This term refers to a change in color suffered by a solid on exposure to light, which is slowly reversed when the solid is subsequently kept in darkness. It was first observed, named and extensively investigated by Marckwald.[82] It is exhibited by over two hundred substances, but as yet little quantitative work has been done. An interesting feature is the occurrence of phototropic fatigue. 3,5-dibenzoyl-2,4,4,6-tetraphenyltetrahydropyran, which is colorless in the dark, becomes violet on exposure to light, especially that of short wave-lengths. It again becomes colorless after some hours or days in darkness. After ten such colorations and decolorations, however, it loses its phototropic properties and its melting point falls from 235-6° to 225°C.[83] In solution, it is insensitive to light, and the colored form when dissolved yields colorless solutions. An occasional instance of phototropy in solution has, however, been reported. Singh [84] observed a green color to develop in chloroform solutions of α-naphthylaminocamphor on exposure to direct sunlight, followed by a much slower reversal in darkness The coloration was accompanied by a large increase in optical rotation. The addition of a trace of sodium ethoxide prevented the appearance of the green color. The results were tentatively attributed to the formation of a compound from the keto and enol modifications.

The phototropy of inorganic compounds of the type $2HgS.HgX_2$ or $2HgS.HgX$ has been attributed [85] to their dissociation into the simple component salts, recombination occurring in darkness with the reëmission of radiant energy.

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[77] Macht, D. I., and Anderson, W. T., Jr., *J. Am Chem. Soc.*, **49**, 2017 (1927)

[78] Macht, D. I., and Krantz, J. C., Jr., *J. Am Pharm Assoc.*, **16**, 106 (1927).

[79] Dailey, H. T., and Benedict, H. C , *J. Am. Chem. Soc.*, **51**, 808 (1929)

[80] Bunker, J. W. M., and Anderson, E. G. E., *J. Biol. Chem* **77**, 473 (1928).

[81] Bond, W. R., and Gray, E. W., *J. Pharm. Exp. Therap.*, **32**, 351 (1928). See also for further details of the controversy, Jones, W. N., *Ann. Botany*, **39**, 651 (1925); Baly, E. C C., and Semmens, E. S., *Nature*, **116**, 817 (1925); Semmens, E. S., *Plant Physiol.*, **1**, 201 (1926); *Nature*, **117**, 821 (1926); Lord Rayleigh, *Nature*, **117**, 15 (1926); Navez, A. E., and Rubenstein, B. B., *J. Biol. Chem.*, **80**, 503 (1928).

[82] Marckwald, W., *Z. physik. Chem.*, **30**, 140 (1899). For reviews, see Gallagher, P., *Bull. soc. chim.*, **29**, 683 (1921) and Chalkley, L., Jr., *Chem. Rev.*, **6**, 217 (1929). Note also Bhatnagar, S. S., Kapur, P. L., and Hashmi, M. S., *J. Indian Chem. Soc.*, **15**, 573 (1938); *Chem Abs.*, **33**, 3698 (1939).

[83] de Carvalho, A. P., *Compt. rend.*, **200**, 60 (1935).

[84] Singh, B. K., *Quart. J. Indian Chem. Soc.*, **1**, 45 (1924); *Chem. Abs.*, **19**, 935 (1925).

[85] Rao, E. L., Varahalu, K., and Narasimhaswami, M. V., *Nature*, **124**, 303 (1929).

PHOTOELECTRIC PHENOMENA

In 1839, Becquerel[86] discovered that when one of two platinum or silver electrodes in dilute sulfuric acid is illuminated, an electromotive force is set up by the cell. That the conductivity of certain substances, notably selenium, is affected by light was, according to Bidwell[87] discovered by Willoughby Smith in 1873. In attempting to explain an observation by Hertz[88] that ultraviolet illumination of a spark gap permits the passage of a longer spark, Hallwachs[89] discovered the emission of negative electricity from a surface irradiated by ultraviolet rays. As pointed out by Hughes and DuBridge,[90] these three phenomena are separate manifestations of photoelectric processes, which all depend upon the ability of light to release electrons from matter.

Historically, the photoelectric effect is of the greatest importance, since it was the study of this phenomenon which enabled Einstein[91] to reveal the fact that the interaction between matter and radiation must be explained in terms of quanta of radiation. The theoretical structure of modern photochemistry is based upon his introduction of the concept which led to the logical development of the photochemical equivalence law. On the other hand, the actual occurrence of a photoelectric effect as a part of the mechanism of photochemical processes is relatively unusual. That air and other gases may be ionized by ultraviolet radiations has long been recognized[92] and at one time it was believed that photoionization might play an important role in photochemical processes. But when the amounts of energy required to ionize the molecules of various gases became known, it became evident that the wave-lengths corresponding to ionization are generally far shorter than those required to bring about most photochemical processes. Only rays passing through fluorite are able to ionize most gases. The required thresholds range from 1300A for nitric oxide to 760A for nitrogen, the halogens having the values chlorine, 940A, bromine, 970A, and iodine, 1230A.[93]

Many investigations have been made of the effects of illumination upon the electrodes of electrolytic or voltaic cells, but these lie beyond the scope of this work.

[86] Becquerel, E., *Compt. rend.*, **9**, 145, 561 (1939); for a recent review, see Stora, C., *J. chim phys.*, **34**, 536 (1937).

[87] Bidwell, S., *Phil. Mag.*, **20**, 178 (1885).

[88] Hertz, H, *Ann. Physik*, **31**, 983 (1887).

[89] Hallwachs, W., *Ann. Physik*, **33**, 301 (1888).

[90] Hughes, A. L., and DuBridge, L. A., "Photoelectric Phenomena," New York, McGraw-Hill Book Co., 1932.

[91] Einstein, A, *Ann. Physik*, **17**, 132 (1905).

[92] Thomson, J. J., *Proc. Cambridge Phil. Soc.*, **14**, 417 (1907); *Chem. Abs*, **2**, 1656 (1908).

[93] See Mackay, C. A., *Phil. Mag.*, **46**, 828 (1923); Morris, J. C., Jr., *Phys Rev.*, **32**, 456 (1928); Hughes, A. L., and DuBridge, L. A., "Photoelectric Phenomena," p. 274, New York, McGraw-Hill Book Co., 1932.

Chapter 17

Reactions of Inorganic Gases: Hydrogen Halides

In Chapter 14 it was shown that a knowledge of the spectrum of a gas is essential to comprehending the reactions which it may undergo under the influence of radiations. Even when apparatus capable of revealing the finer structure of the molecular spectra is not available, crude spectrographs may furnish an indication of the wave-length regions within which the gas absorbs and will therefore give some indication of the regions within which photochemical reactions can occur. A brief discussion of the manner in which absorption measurements are made will first be given. Then in the discussions of the individual reactions, the absorption spectrum of each of the components will be described in order that the findings of spectroscopy as to the nature of the possible primary processes may furnish a guide for a critical appraisal of the various speculations proposed in explanation of the reported observations on the kinetics of the reactions.

The Measurement of Ultraviolet Absorption Spectra of Gases or Liquids

Since this is not a text of laboratory procedure, only principles and not details of technique will be mentioned. In general, the methods are similar to those commonly employed in the visible region. Ultraviolet light, from a spark source or hydrogen discharge tube, is divided into two parallel paths, one of which passes directly into the spectrograph; the other passes through a cell containing the gas or the solution the absorption of which is to be measured. (If the absorption of a solution is being studied, the first beam should pass through a cell containing the pure solvent.) The two spectra are then photographed side by side. Several exposures are made on adjacent portions of the photographic plate, the intensity of the comparison beam being varied to a known extent in each. Methods employed in photometers for decreasing the intensity of the comparison beam include the interposition of rotating sectors which vary in known manner the duration of intermittent exposures, the use of wire screens[1] or calibrated platinum wedges deposited on quartz, Nicol polarizing prisms or variations of the aperture admitting the comparison beam (Spekker method of Adam Hilger, Ltd.). It would theoretically be best to secure the variation in intensity by varying the distance from the source, but this is not feasible when a photographic method is employed and it has rarely been used in other methods.[2]

In each of the series of double spectra, however obtained, there are located (visually or microphotometrically) the wave-length regions at which there is agreement between the intensity of the light passing through the absorption cell and that coming directly from the source. The wave-lengths corresponding to various positions along the spectrum are determined by a simultaneously photographed scale embodied in the instrument or located by the use of known lines of the source as landmarks. Most of the methods in common use, particularly for work with solutions, involve merely a direct visual matching of the intensities upon the photographic plate variously illuminated.

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[1] Winther, C., *Z. wiss. Phot.*, **22**, 125 (1923); Landsberg, G. S., *Z. Physik*, **46**, 106 (1927).

[2] Schaefer, K., *Z. angew. Chem.*, **33**, 25 (1920).

A method in which the light intensity was kept constant and the path of absorbent traversed, or the concentration of the absorbing solution, was varied, was introduced by Henri.[3] Refinements in this method have been introduced by de Lazlo.[4] A simple method employing only a quartz spectrograph and no photometer has been employed by Loofbourow.[5] Methods have also been devised employing but one beam of light, so that instead of matching intensities on a photographic plate, the energy of the beam is measured by a thermopile or, more usually, a photoelectric cell and accessory apparatus, with the absorption cell in the beam and without it. Among photoelectric spectrophotometric methods are those of Hogness, Zscheile and Sidwell.[6] Automatic recording devices have also been constructed. A continuous representation of the absorption curve of a rapidly changing system can be obtained by the aid of a cathode-ray oscillograph, according to Holiday and Smith.[7] The fine structure of the absorption spectra of gases is obtained by micrometric tracings of photographed spectra.[8]

In the absorption curve of a substance there is plotted against wave-lengths as abscissae the ratio of the light passing through the absorbing substance (I_x) to that incident upon it (I_0). This ratio is given by the logarithmic relation $I_x/I_0 = e^{-kcd}$, in which c is the concentration of a solution (or pressure of a gas). d the thickness of the absorbing layer and k is a constant characterizing the absorption of the substance at the wave-length in question. A plot of k against the wave-lengths gives graphically the absorption of the substance throughout the spectral range investigated. k is known as the absorption coefficient, and varies with the wave-length. The numerical value of k is obtained by dividing the product cd into the natural logarithm of the ratio of I_0/I_x. In practice, most workers employ the more convenient common logarithms. The terms "extinction coefficient" and "absorption coefficient" are rather indiscriminately employed to designate the values obtained by the use of either logarithmic base. In general, German authors follow Kayser in using the term "absorption coefficient" for values based on natural logarithms and English workers follow Bunsen and Roscoe in using "extinction coefficient" for values based on the use of logarithms to the base ten. The distinction in terms is by no means universally observed.

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[3] See Ley, H., and Volbert, F., *Z. wiss. Phot.*, **23**, 41 (1924).

[4] de Lazlo, H., *J. Phys. Chem.*, **32**, 505 (1928).

[5] Loofbourow, J. R., *Bull. Basic Sci. Research*, **5**, 46 (1933).

[6] Hogness, T. R., Zscheile, F. P., Jr., and Sidwell, A. E., Jr., *J. Phys. Chem.*, **41**, 379 (1937).

[7] Holiday, E. R., and Smith, F., *Nature*, **134**, 102 (1934).

[8] See Harrington, E. A., *J. Opt. Soc. Am.*, **16**, 211 (1928); Gull, H. C., and Martin, A. E., *J. Sci. Instruments*, **12**, 379 (1935).

The following bibliography includes but a few of the more important papers on the measurement of absorption spectra and their applications to the study of constitution. A considerable proportion of them, indicated separately, are concerned primarily with the limitations of the photographic method because of the failure of the relation between the intensity of the light and the blackening of the plate.

van Halban, H., and Eisenbrand, J., *Proc. Roy. Soc.*, **116A**, 153 (1927); *Z. wiss. Phot.*, **25**, 138 (1928). Baly, E. C. C., and Riding, R. W., *Proc. Roy. Soc.*, **113A**, 709 (1927). Schaum, K., and Kellner, H. M., *Z. wiss. Phot.*, **24**, 85 (1926). Fromherz, H., *Z. physik. Chem.*, **1B**, 301 (1928). Gage, F. H., *J. Sci. Instruments*, **6**, 256 (1929). Conrad-Billroth, H., *Z. physik. Chem.*, **14B**, 122 (1931). Schlessinger, M., *Biochem. Z.*, **235**, 70 (1931). Ley, F., and Volbert, F., *Z. physik. Chem.*, **130**, 308 (1927). Twyman, F., *Proc. Phys. Soc. (London)*, **45**, 1 (1933). Ginsel, L. A., *Physica*, **3**, 578 (1936). von Halban, H., Kortüm, G., and Szigetti, B., *Z. Elektrochem.*, **42**, 628 (1936). Miller, E. S., *Plant Physiol.*, **12**, 667 (1937). Albers, V. M., and Knorr, H. V., *J. Opt. Soc. Am.*, **28**, 121 (1938). Deck, W., *Helv. Phys. Acta*, **11**, 1 (1937). Shlaer, S., *J. Opt. Soc. Am.*, **28**, 18 (1938). P. J. Kippen Zonen, *J. Sci. Instruments*, **15**, 141 (1938). Papers dealing with the limitations of the reciprocity law and the Schwarzschild law in photographic materials: Harrison, G. R., *J. Opt. Soc. Am.*, **11**, 341 (1925); **19**, 267 (1929). Kellner, H. M., *Z. wiss. Phot.*, **24**, 41, 79 (1926). Dorgelo, H. B., *Physik. Z.*, **26**, 756 (1925). Fabry, C., *Phot. J.*, **66**, 328 (1926). Jones, L. A., and Hall, V. C., *J. Opt. Soc. Am.*, **13**, 443 (1926). Webb, J. H., *J. Opt. Soc. Am.*, **23**, 316 (1933). Mees, C. E. K., *J. Opt. Soc. Am.*, **23**, 229 (1933). Harvey, A., *Science Progress*, **27**, 650 (1933). Kinele, H., *Naturwiss.*, **23**, 762 (1935). Pestemer, M., and Schmidt, G., *Monatsh.*, **69**, 399 (1936). Lambrey, M., and Corbière, J., *Compt. rend.*, **201**, 1351 (1935). van Kreveld, A., and Ornstein, L. S., *Proc. Acad. Sci. Amsterdam*, **39**, 478 (1936). de Langhe, J. E., *Physica*, **3**, 904 (1936). Kiss, A., and Gerendas, M., *Acta Lit. Sci. Regiae Univ. Hung. Francisco-Josephinae, Sect. Chem. Mineral. Phys.*, **5**, 153 (1937); *Chem. Abs.*, **32**, 1577 (1938).

THE FORMATION AND DECOMPOSITION OF THE HYDROGEN HALIDES

The Decomposition of Hydrogen Iodide. According to Rollefson and Booher,[9] the first mention of this reaction was by Lemoine.[10] Also, the reaction was early studied by Bodenstein.[11] Warburg[12] found a quantum yield of approximately two for the wave-lengths 2070, 2530 and 2820A. In Chapter 12 it was shown that this observation could be accounted for equally well by either the mechanism of primary dissociation proposed by Warburg or of primary excitation of the hydrogen iodide molecule proposed by Stern and Volmer. Attempts to decide between the two by Bodenstein on the basis of kinetic measurements under varied experimental conditions, especially in the presence of foreign gases, were inconclusive. The data which eventually showed the correctness of the Warburg mechanism were predominantly physical and, as discussed in Chapter 14, came from the finding that the absorption spectrum of hydrogen iodide is continuous. At this point, we may consider in more detail the spectroscopic evidence regarding the absorption not only of hydrogen iodide but also of the products of the reaction, hydrogen and iodine.

Tingey and Gerke[13] found the absorption of hydrogen iodide to be entirely continuous and to begin at 3320A, corresponding to 86 kcal.; Coehn and Stuckardt[14] had previously placed this value at 3340A. It has been generally assumed[15] that the iodine atom produced in the dissociation is excited as in the case of the halogen from hydrogen chloride and hydrogen bromide. The energy of excitation of iodine is, from its atomic spectrum, 21.5 kcal. This, when subtracted from the energy corresponding to the long-wave threshold of the absorption spectrum 86 kcal. leaves 64.5 kcal., in fair agreement with the heat of dissociation of HI into normal atoms, 69 kcal. Goodeve and Taylor[16] calculated a potential energy curve for the upper state from the eigenfunction of the ground state and their own observations of the extinction values. Rollefson and Booher[17] found the absorption to extend as far as 3900A at least, and gave evidence that at 4120A, dissociation into normal atoms can occur; at 3120A, the iodine atom may be excited. Datta[18] places the absorption limit at 4040A.

Hydrogen. The fact that hydrogen absorbs only in the extreme ultraviolet range eliminates this substance as an absorbing component which might affect either the dissociation of hydrogen iodide or the combination of hydrogen and iodine. Dieke and Hopfield[19] found that in a 100 cm. layer at pressures of 2 to 50 mm. of mercury, hydrogen does not absorb wave-lengths longer than 1115A. Below this, it exhibits two band systems, the members of both of which converge at 849.4A to a region of continuous absorption corresponding to dissociation into a normal and an excited atom.

Iodine. Observations by Dymond[20] of the short wave-length limit of fluores-

[9] Rollefson, G. K., and Booher, J. E., *J. Am. Chem. Soc.*, **53**, 1728 (1931).

[10] Lemoine, G, *Ann. Chim. Phys.*, **12**, 145 (1877).

[11] Bodenstein, M., *Z. physik. Chem.*, **22**, 23 (1897); **85**, 329 (1913); Bodenstein, M., and Lieneweg, F., *Z. physik. Chem.*, **119**, 123 (1926).

[12] Warburg, E., *Sitzb. preuss. Akad. Wiss.*, 314 (1916); 300 (1918).

[13] Tingey, H. C., and Gerke, R. H., *J. Am. Chem. Soc.*, **48**, 1838 (1926); see also Bonhoeffer, K. F., and Steiner, W., *Z. physik. Chem.*, **122**, 287 (1926); Lewis, B., *Nature*, **119**, 493 (1927).

[14] Coehn, A., and Stuckardt, K., *Z. physik. Chem.*, **91**, 722 (1916).

[15] Lewis, B., *Proc. Nat. Acad. Sci.*, **13**, 720 (1927); *J. Phys. Chem.*, **32**, 270 (1928).

[16] Goodeve, C. F., and Taylor, A. W. C., *Proc. Roy. Soc.*, **154A**, 181 (1936).

[17] Rollefson, G. K., and Booher, J. E., *J. Am. Chem. Soc.*, **53**, 1728 (1931).

[18] Datta, A. K., *Z. Physik*, **77**, 404 (1932).

[19] Dieke, G. H., and Hopfield, J. J., *Phys. Rev.*, **30**, 400 (1927); *Z. Physik*, **40**, 299 (1926).

[20] Dymond, E. G., *Z. Physik*, **34**, 553 (1925).

cence were important in establishing the generally accepted interpretation of continuous spectra as indicative of dissociation. Iodine vapor exhibits bands which converge at 4989A to a continuous absorption region.[21] Fluorescence can be induced by wave-lengths longer than the convergence limit but cannot be observed in iodine vapor irradiated by wave-lengths within the continuous region. The dissociation produces a normal and an excited iodine atom.[22]

Extinction values have been given by Vogt and Königsberger[23] and, more recently, by Rabinowitsch and Wood.[24] The effect of varying the pressure of the iodine vapor has been studied by Perot and Collinet,[25] and the influence of foreign gases on the color of iodine vapor reported by Wright and McGregor.[26] The extinction coefficients drop off toward shorter wave-lengths in the continuous region. In the region below 2763A, iodine vapor exhibits a new region of banded absorption, the interpretation of which is not yet clear.[27]

By spectroscopic methods, Rabinowitsch and Wood[28] measured the quantum yield of the dissociation of iodine in the presence of foreign gases in three spectral regions. If the yield is unity in the continuum, it is 1.14 in the band region immediately on the long-wave side, and 1.10 at a point in the band region further from the limit. This indicates that all excited molecules dissociate by collisions with foreign molecules. Therefore, the quenching of the fluorescence is not due to the process $I_2^* + X \rightarrow I_2 + X$, but rather to $I_2^* + X \rightarrow I + I + X$. Quenching usually occurs at the first collision of an excited molecule with a foreign molecule, except in the case of helium which requires ten or more collisions before dissociation results. The atoms recombine mainly at the walls at low pressures. Under these conditions dissociation increases with the pressure. At higher pressures, however, the recombination occurs as a homogeneous reaction in the gas phase. The transition occurs sharply at 250 mm. in helium and 40 mm. in carbon dioxide. The dissociation is then proportional to the square root of the light intensity and to the inverse square root of the pressure, in accordance with the theoretical expression for recombination by three-body collisions. One double collision in 530 is a recombining one in helium and one in 50 in carbon dioxide at atmospheric pressure. The efficiency of the third body increases with its molecular size and with the intensity of the molecular fields of the colliding particles.

To decide between the mechanisms proposed (Chapter 12) for the decomposition of hydrogen iodide, Bonhoeffer and Farkas[29] studied the reaction at low pressures at which, were the reaction due to excited molecules, some re-radiation of the energy of excitation would be expected since the period between deactivating collisions would be longer than the life of the excited state. Since they could detect no fluorescence, it was concluded that the mechanism of Warburg (dissociation) must apply. Furthermore, exposure to light resulted in a fall of pressure which could be attributed only to the adsorption of free iodine atoms on the walls of the vessels. The same fall in pressure was also observed during the irradiation of hydrogen bromide.

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[21] Mecke, R., *Ann Physik*, **71**, 104 (1923); Brown, W. G., *Phys. Rev.*, **38**, 709 (1931).

[22] Turner, L. A., *Phys. Rev.*, **27**, 397 (1926).

[23] Vogt, K., and Königsberger, J , *Z. Physik*, **13**, 292 (1923).

[24] Rabinowitsch, E., and Wood, W. C., *Trans. Faraday Soc.*, **32**, 540 (1936).

[25] Perot, A., and Collinet, M., *Compt. rend.*, **180**, 2030 (1925).

[26] Wright, R., and McGregor, T., *J. Chem. Soc.*, 1364 (1929).

[27] Pringsheim, P., and Rosen, B., *Z. Physik*, **50**, 1 (1928); Sponer, H , and Watson, W., *Ibid.*, **56**, 184 (1929); Kimura, M., and Miyanishi, M., *Sci. Papers Inst. Phys. Chem. Research Tokyo*, **10**, 33 (1929). Further recent data on the absorption of iodine, particularly in the long-wave regions, have been given by Hirschlaff, E., *Z. Physik*, **75**, 315 (1932); Agarbiceanu, T., *Compt. rend.*, **194**, 702 (1932); Kondratjev, V., and Polak, L., *Physik. Z. Sowjetunion*, **4**, 764 (1933); Skorko, E., *Acta Phys. Polonica*, **3**, 191 (1934); Warren, D., *Phys. Rev.*, **47**, 1 (1935). The Budde effect differs from that of the other halogens in being proportional to the light intensity rather than to its 0.5 power. Narayana, T. S., *Indian J. Physics*, **9**, 111, 117 (1934); *Chem. Abs.*, **29**, 2847 (1935).

[28] Rabinowitsch, E., and Wood, W. C , *J. Chem. Physics*, **4**, 358, 497 (1936).

[29] Bonhoeffer, K. F., and Farkas, L., *Z physik. Chem.*, **132**, 235 (1928).

Wave-lengths between 3000 and 2200A cause the complete decomposition of hydrogen iodide.[30] The velocity is independent of temperatures below 120°C.; it is lowered by addition of either iodine vapor or of an excess of hydrogen. At the beginning of reaction, the velocity remains constant for a time, then falls to that of a unimolecular reaction, and later falls again. The falling off in the rate toward the end of the decomposition is hastened when the initial pressure of hydrogen iodide is high and the temperature low. The initial reaction velocity appeared to increase approximately in proportion to the initial concentration of hydrogen iodide. Quantum yields somewhat higher than those of Warburg have been reported by Lewis,[31] his values being 2.36 for the 2080A and 2.35 for the 2530A zinc lines. The product of the intermediate reaction $H + HI \rightarrow H_2 + I$ is 25 per cent para-hydrogen at room temperatures. At 170°Abs. the hydrogen produced contains 2 per cent more para-hydrogen than does normal hydrogen.

Studies of the photochemical combination of hydrogen and iodine have been made by Coehn and Stuckardt,[32] who found that reaction can occur only in the ultraviolet region, and by Sasaki and Nakamura.[33] The latter workers found no combination could be induced by radiations longer than 3100A. It is suggested that hydrogen atoms may be produced by collisions of the second kind between hydrogen molecules and iodine molecules excited by the absorption of the 1800A line, although dissociation of iodine might be expected. The production of hydrogen atoms is essential that the reaction may go at ordinary temperatures since the reaction $I + H_2 \rightarrow HI + H$ is too endothermic to proceed. There is some evidence that the photocombination occurs under the influence of visible light at temperatures of 430-466°C.[34]

Other Halogen Hydrides.[35] Berthelot and Gaudechon[36] found that, as in the case of thermal decompositions, the stabilities of the hydrogen halides in light decrease with increasing atomic weights of the halogens. Those substances which require high temperatures for thermal decomposition require the shortest wavelengths in the ultraviolet. For the decomposition of hydrogen chloride, wavelengths shorter than 2000A are required to produce even a slow decomposition. Under similar conditions, hydrogen bromide is rapidly and completely decomposed. Coehn and Stuckardt[37] effected reactions of hydrogen halides from both

Table 19.—Photostationary States of Hydrogen Halides.

Acid	In quartz (2200A)	In Uviol glass (2500A)	In Jena glass (3000A)?
Hydriodic	92.2	100	100
Hydrobromic	100	about 20	0
Hydrochloric	0.42	0	0.

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[30] Trautz, M., and Scheifele, B., *Z. wiss. Phot.*, **24**, 177 (1926).

[31] Lewis, B., *Proc. Nat Acad. Sci.*, **13**, 720 (1927); *J. Phys. Chem* , **32**, 270 (1928).

[32] Coehn, A., and Stuckardt, K., *Z. physikal. Chem.*, **91**, 722 (1916).

[33] Sasaki, N., and Nakamura, K., *Anniversary Volume Dedicated to M. Chikashige (Kyoto Imp. Univ.)* 299 (1930); *Chem. Abs.*, **25**, 2921 (1931).

[34] Lewis, B., and Rideal, E. K., *J. Am. Chem. Soc.*, **48**, 2553 (1926).

[35] Almost no work has been reported on the combination of hydrogen and fluorine. See, however, Bodenstein, M., and Jockersch, H., *Z. anorg. Chem.*, **231**, 24 (1937).

[36] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **156**, 889 (1913); *J. Chem. Soc* , **104** (II), 369 (1913).

[37] Coehn, A., and Stuckardt, K., *Z. physik. Chem.*, **91**, 722 (1916); *Chem. Abs.*, **11**, 749 (1917).

sides of the equilibrium in vessels of quartz, Uviol glass and Jena glass. These glasses roughly delimited three spectral ranges. The percentage decomposition of each acid at equilibrium is listed in Table 19.

The reactions of hydrogen bromide are very well adapted for the presentation of the method devised by Bodenstein for the treatment of the kinetics of photochemical reactions in general and will be discussed in detail as representative of the methods employed in studying photochemical mechanisms. The case of hydrogen chloride is so complicated that a separate chapter is devoted to its consideration. Before proceeding to a consideration of kinetics, the essential data on the absorption spectra of bromine vapor and hydrogen bromide will be presented.

Absorption of Bromine. In the visible range there is absorption from about 6000A to 3500A, the maximum occurring at about 4100A.[38] Bands from about 5700A converge to a limit at 5107A.[39] At shorter wave-lengths the absorption is continuous, implying a dissociation into a normal atom and one in a metastable state with excitation energy of 10.5 kcal.[40] In the ultraviolet region, bromine vapor at higher pressures exhibits a continuous region from 2700A to the limit of observations at 1560A.[41] Brown[42] has found another band region between 7500 and 6400A, the bands of which apparently converge to a limit indicative of dissociation into two normal atoms. (A dissociation energy of 45.2 kcal. corresponds to 6290A.) Other absorption studies were made by Barratt and Stein,[43] Nakamura,[44] and Hays.[45] The excitation of fluorescence within the range 5000-5600A has been studied by Daure.[46] Wave-lengths in the continuous band below 5000A excite no fluorescence.

Absorption by Hydrogen Bromide. Hydrogen bromide absorbs continuously in the shorter ultraviolet.[47] Tingey and Gerke[48] found continuous absorption to begin at a wave-length which varies with the mass of gas studied, approaching 2640A as a limit as the mass of gas is increased. Coehn and Stuckardt had given 2650A. The absorption limit was unaffected by temperature over the range 25° to 400°C. Datta, however, placed the long-wave threshold at 3260A. The formation of free atoms has been established by Bonhoeffer and Farkas.[49] Goodeve and Taylor[50] believe the molecule dissociates into atoms in normal states. Trivedi's spectroscopic value for the dissociation energy is 92 kcal.[51] There have been but few studies of the decomposition of hydrogen bromide but the work of Warburg[52] is so conclusive that it is generally accepted that the primary process, as in the case of hydrogen iodide is one of photodissociation. The quantum yield is 2.08 at 2070A and 2.00 at 2530A.

Combination of Hydrogen and Bromine. At ordinary temperatures, this reaction occurs to but a very slight extent, Pusch[53] finding that the absorption of a thousand quanta produces only one molecule of hydrogen bromide. At temperatures of 100° to 200°C., Kastle and Beatty[54] found a reaction to occur. At still higher temperatures (200-300°C.) a thermal reaction occurs in the dark. The kinetics of the dark reaction have been studied by Bodenstein and Lind.[55] Interpretation of this reaction given by Christiansen,[56] Polanyi[57] and Herzfeld[58] involved the thermal dissociation of bromine into atoms.[59]

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[38] Bovis, P., *J. Phys. Radium*, **10**, 267 (1929); Kuhn, H., *Z. Physik*, **39**, 77 (1926).

[39] Brown, W. G., *Phys. Rev.*, **38**, 1179 (1931).

[40] Turner, L. A., *Phys. Rev.*, **27**, 397 (1926).

[41] Cordes, H., and Sponer, H., *Z. Physik*, **63**, 334 (1930).

[42] Brown, W. G , *Phys. Rev.*, **39**, 777 (1932). For the absorption of liquid bromine, see Porret, D., *Proc. Roy. Soc.*, **A162**, 414 (1937).

[43] Barratt, S., and Stein, C. P., *Proc. Roy. Soc.*, **122**, 582 (1929).

[44] Nakamura, G., *Mem. Coll. Sci. Kyoto*, **9**, 335 (1926); *Chem. Abs.*, **21**, 2431 (1927).

[45] Hays, M. B., *J. Frank. Inst.*, **208**, 363 (1929).

[46] Daure, P., *Compt. rend.*, **183**, 31 (1926).

[47] Coehn, A., and Stuckardt, K., *Z. physik. Chem.*, **91**, 737 (1916); Warburg, E., *Berlin Akad. Ber.*, 314 (**1916**); 300 (**1918**); Datta, A. K., *Z. Physik*, **77**, 404 (1932).

[48] Tingey, H. C., and Gerke, R. H , *J. Am. Chem. Soc.*, **48**, 1844 (1926).

[49] Bonhoeffer, K. F., and Farkas, L., *Z. physik. Chem.*, **132**, 235 (1928).

[50] Goodeve, C. F., and Taylor, A. W. C., *Proc. Roy. Soc.*, **A152**, 221 (1935).

[51] Trivedi, H., *Proc. Natl. Acad. Sci. India*, **6**, 29 (1936); *Chem. Abs.*, **30**, 4760 (1936).

[52] Warburg, E., *Berlin Akad. Ber.*, 314 (**1916**); 300 (**1918**).

From the absorption data, it is evident that the photoreaction also proceeds by a mechanism involving free bromine atoms. That the quantum yield exceeds two only at high pressures of hydrogen and that the hydrogen-bromine mixture is insensitive to light at ordinary temperatures are explained on the basis that the reaction

$$Br + H_2 \longrightarrow HBr + H$$

is endothermic. The necessary activation energy can be supplied only thermally at high temperatures.[60]

Bodenstein and Lütkemeyer[61] studied the reaction rate spectrophotometrically by measuring the disappearance of the bromine. They employed temperatures of 160-218°, and irradiated the mixture with moderately intense light from a tungsten arc. The combination takes place with a velocity about 300 times as great as that of the dark reaction at the same temperature. They found also that, under conditions of weak absorption and at the beginning of the reaction, the rate of formation of hydrogen bromide was proportional to the concentration of hydrogen and to the square root of the bromine concentration and the square root of the absorbed energy. When absorption is complete, and in later stages of the reaction when a stationary concentration of bromine atoms has been reached, the rate of the reaction is expressed by

$$\frac{d(\mathrm{HBr})}{dt} = \frac{2k_2(\mathrm{H_2})\sqrt{\dfrac{\text{No. of quanta absorbed}}{k_5}}}{1 + \dfrac{k_4(\mathrm{HBr})}{k_3(\mathrm{Br_2})}}$$

The various k values employed refer to the rate constants in the numbered equations which can be set down for the primary process and for the reactions of the products of this reaction with all other substances present. In this case these reactions are

$$\begin{array}{ll}
1. & Br_2 + h\nu \longrightarrow 2Br \\
2. & Br + H_2 \longrightarrow HBr + H - 16.2 \text{ kcal.} \\
3. & H + Br_2 \longrightarrow HBr + Br + 40.5 \\
4. & H + HBr \longrightarrow H_2 + Br + 16.2 \\
5. & Br + Br \longrightarrow Br_2 + 45.2
\end{array}$$

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[53] Pusch, L., *Z. Elektrochem.*, **24**, 336 (1918).

[54] Kastle, J. H., and Beatty, W. A., *Am. Chem. J.*, **20**, 159 (1898).

[55] Bodenstein, M., and Lind, S. C., *Z. physik. Chem.*, **57**, 168 (1906).

[56] Christiansen, J. A., *Kgl. Danske Videnskab Selskab, Math-fys. Medd.*, **1**, 14 (1919); *Chem. Abs.*, **14**, 1085 (1920).

[57] Polanyi, M., *Z. Elektrochem.*, **26**, 50 (1920).

[58] Herzfeld, K. F., *Z. Elektrochem.*, **25**, 301 (1919); *Ann. Physik*, **59**, 635 (1919).

[59] See, however, Skrabal, A., *Ann. Physik*, **82**, 138 (1927).

[60] Lewis, B., and Rideal, E. K., *J. Am. Chem. Soc.*, **48**, 2553 (1926). Compare the analogous chlorine reactions in the next chapter.

[61] Bodenstein, M., and Lütkemeyer, H., *Z. physik. Chem.*, **114**, 208 (1924).

The plausibility of each of the secondary reactions is then considered. Exothermic reactions are always admitted, although in the case of certain recombinations of free atoms the reaction is not possible except as a result of three-body collisions involving a foreign inert gas or a wall reaction. Endothermic reactions are excluded or admitted, depending upon the possibility of securing the necessary activation energy thermally in a reasonable fraction of collisions at the temperature of the reactants.

The intermediate products are considered to exist (except at the beginning of the irradiation period) in stationary concentrations, reactions leading to their removal summing up to a removal rate equal to the sum of the rates of the reactions by which they are formed. Thus, in this case,

$$\frac{d(\mathrm{Br})}{dt} = 2k_1(\mathrm{Br}_2) + k_3(\mathrm{H})(\mathrm{Br}_2) + k_4(\mathrm{H})(\mathrm{HBr})$$

$$= \frac{-d(\mathrm{Br})}{dt} = k_2(\mathrm{Br})(\mathrm{H}_2) + 2k_5(\mathrm{Br}^2)$$

Similarly, for the stationary concentration of H atoms,

$$k_3(\mathrm{H})(\mathrm{Br}_2) = k_4(\mathrm{H})(\mathrm{HBr}) + k_2(\mathrm{Br})(\mathrm{H}_2).$$

Solution of these simultaneous equations makes it possible to express the stationary concentrations of the bromine atoms and of hydrogen atoms in terms of rate constants and the concentrations of hydrogen, bromine and hydrogen bromide molecules. Thus, by subtracting the second from the first equation and solving for (Br), the value k_1/k_5 (Br_2) is obtained. Solving the second equation alone gives for the hydrogen atom concentration

$$\frac{k_2(\mathrm{Br})(\mathrm{H}_2)}{k_3(\mathrm{Br}_2) + k_4(\mathrm{HBr})}$$

and by substituting in this the value just found for the bromine atom concentration, the stationary H atom concentration becomes

$$[\mathrm{H}] = \frac{k_2(\mathrm{H}_2)\sqrt{\frac{k_1}{k_5}(\mathrm{Br}_2)}}{k_3(\mathrm{Br}_2) + k_4(\mathrm{HBr})}$$

The secondary reactions leading to the formation of hydrogen bromide are next summed up and those leading to its destruction deducted.

$$\frac{d(\mathrm{HBr})}{dt} = k_2(\mathrm{Br})(\mathrm{H}_2) + k_3(\mathrm{H})(\mathrm{Br}_2) - k_4(\mathrm{H})(\mathrm{HBr})$$

By substituting the calculated values for the stationary states of hydrogen and bromine atoms and simplifying algebraically, it is then possible to arrive at an equation which will express the overall kinetics of the reaction. In this case the equation is

$$\frac{d(\mathrm{HBr})}{dt} = \frac{2\mathrm{k}_2(\mathrm{H}_2)\sqrt{\frac{k_1}{k_5}(\mathrm{Br}_2)}}{1 + \frac{k_4(\mathrm{HBr})}{k_3(\mathrm{Br}_2)}}$$

In deriving this expression the formation of bromine atoms was assumed to occur thermally. When formation occurs by the absorption of light as in equation (1), the stationary concentration of bromine atoms is given by $(\mathrm{Br}) = \sqrt{\frac{n}{k_5}}$, in which n is the number of quanta absorbed per second. In the final equation the radical $\sqrt{\frac{k_1}{k_5}(\mathrm{Br}_2)}$ must be replaced by $\sqrt{\frac{n}{k_5}}$. The final result agrees with the observations of Bodenstein and Lütkemeyer that the rate is proportional to the square root of the light intensity at complete absorption. In this expression, it is implied that at the start of the reaction, before hydrogen bromide has formed to an appreciable extent, the denominator becomes unity and the rate is proportional to the hydrogen concentration and the square root of the light intensity. This was observed. Furthermore, if not all of the light is absorbed, the rate also is proportional to the square root of the concentration of the absorbing component, bromine. This also was observed. An examination of the derivation of the rate equation reveals why it is that in reactions involving the dissociation of a molecule by light, the square root of the intensity (or of the absorbing component concentration) so frequently enters the rate expression. It may be noted that in the case of this reaction the derivation was made on the basis of a mechanism for the dark reaction, which was found to give agreement with the expression for the kinetic data of Bodenstein and Lind for the thermal reaction;[62] the necessary modification to make the equation express the photochemical reaction was made subsequently by Bodenstein and Lütkemeyer. The effect of hydrogen bromide in retarding the reaction, as indicated in the denominator, is due to its ability to remove hydrogen atoms by reaction (4). The greater speed of the photochemical reaction is due to the greater stationary concentration of bromine atoms produced by light as compared to those produced thermally at the same temperature (in the range studied). The temperature coefficient of the photoreaction was found to be 1.5 and that of the dark reaction 2.0. From the similarity of mechanisms it was found possible to calculate either temperature coefficient from the other. The value of this coefficient for the photoreaction is due to reaction (3); the temperature coefficient of the dark reaction involves also the thermal dissociation of bromine molecules. The value of 1.5 for the light reaction indicated an activation energy of 17.6 kcal.

The second term in the denominator of either the photo- or thermal reaction rate equation involves a ratio of k_4/k_3. In the thermal reaction this is about 1/10 and independent of temperature. Bodenstein and Jung[63] found the ratio 1/8.4 for experiments both in strong light at room temperature and at 302° in darkness. This independence of the ratio over a wide temperature range indicated that reactions (3) and (4) require no activation energy. The heat of a reaction is the difference between the activation energies of the forward and reverse reactions. As (4) is the reverse of (2) and as (4) has a zero activation energy, the activation energy found for (2) from the temperature coefficient of the light reaction must also be the heat of reaction (2). Using this value, Bodenstein and Jung combined it with the heats of certain other known reactions in order to calculate a value for the heat of dissociation of hydrogen of 107 kcal. This has subsequently been corrected by the use of a better value for one of the reactions they use, to give 103.6 kcal, which is in good agreement with the spectroscopic value 101.9 kcal.

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[62] Bodenstein, M., and Lind, S. C., *Z. physik. Chem*., **57**, 168 (1906).

[63] Bodenstein, M., and Jung, G., *Z. physik. Chem*., **121**, 127 (1926).

Still other information was derived by Bodenstein and Lütkemeyer from their data. Division of the photo rate equation by the dark rate equation gives for the quotient of the observed rates

$$\frac{I_0}{k_6} \Big/ \frac{k_1(\mathrm{Br}_2)}{k_5}$$

The ratio k_1/k_5 was known from the work of Bodenstein and Cramer[64] on the thermal equilibrium constant for the dissociation of bromine. It was therefore possible to calculate k_5. They found in this way that only about one in 800 of the collisions between bromine atoms leads to the formation of molecules. Furthermore this figure appeared to be independent of the temperature and total pressure. Briers and Chapman[65] calculated the mean life of the bromine atoms to be 0.063 second. That the removal rate of bromine atoms should be independent of pressure was unexpected in view of the necessity of three-body collisions for recombination and led Jost and Jung[66] to a study of the effect of variation of total pressure over a wide range on the concentration of bromine atoms and therefore also upon the rate of the reaction. The result was the finding that the reaction velocity is inversely proportional to the square root of the total pressure. An explanation of the apparent discrepancy between these results and those of Bodenstein and Lütkemeyer was given by Bodenstein, Jost and Jung.[67] They pointed out that at low pressures the effects of diffusion of the bromine atoms to the walls where recombination could occur had to be taken into account. At low pressures and weak light intensities (*i.e.*, low concentration of bromine atoms) the rate of formation of hydrogen bromide was found to be proportional to the light intensity rather than to its square root. Jost[68] also found that the formation of hydrogen bromide can be brought about by light of wave-lengths greater than 5107A. and therefore in the banded region of the absorption spectrum of bromine. Here the excited bromine molecules yield bromine atoms on collision with other molecules. The bromine atoms recombine in triple collisions and may also be destroyed on the walls, so that the latter have a characteristic effect on the reaction velocity. The activated bromine atoms formed in the primary reaction affect the reaction velocity in the same manner as unactivated ones because they suffer deactivation before they can react. The velocity constants of the single reactions involved in the formation of hydrogen bromide were recalculated from these data and found in agreement with theory.

Ritchie[69] studied the effect of inert gases on the removal of bromine atoms as affecting the rate of the hydrogen bromide formation at 200°C., the results applying either to the thermal or the light reaction. Under conditions favoring the removal of the atoms to the wall, acceleration of the reaction was produced by foreign gases in the order $CCl_4 > CO_2 > N_2$ and $O_2 > A > H_2$ and He. When the removal was primarily by triple collisions in the gas phase, the efficiency was in the order $CO_2 > O_2 > N_2 > A > He > H_2$. Rabinowitsch and Lehmann[70] find the velocity of homogeneous recombination in the presence of helium to vary inversely with the square root of pressure in accordance with the three-body mechanism, and not according to a conceivable mechanism involving the bromine molecule. At atmospheric pressure, about one double collision in 1300 leads to recombination; this is of the order of the total number of triple collisions expected. Argon and nitrogen are more effective than helium in promoting recombination of bromine atoms.[71]

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[64] Bodenstein, M., and Cramer, F., *Z. Elektrochem.*, 22, 327 (1916).

[65] Briers, F., and Chapman, D. L., *J. Chem. Soc.*, 1802 (1928).

[66] Jost, W., and Jung, G., *Z. physik. Chem.*, 3B, 83 (1929).

[67] Bodenstein, M., Jost, W., and Jung, G., *J. Chem. Soc.*, 1153 (1929).

[68] Jost, W., *Z. physik. Chem.*, 134, 92 (1928).

[69] Ritchie, M., *Proc. Roy. Soc.*, 146A, 828 (1934); Hilferding, K., and Steiner, W., *Z. physik. Chem.*, B30, 399 (1935).

[70] Rabinowitsch, E., and Lehmann, H. L., *Trans. Faraday Soc.*, 31, 689 (1935).

Armour and Ludlam[72] state that in a streaming mixture of hydrogen and bromine vapor irradiated by the 1850A line of an aluminum spark less than 1 per cent (by weight) of the bromine enters into combination. This was unaltered by a ten-fold variation of the intensity.

It may be noted that Lewis and Rideal believed the reaction to be inhibited by extreme drying. Bodenstein and Jost[73] however, consider this to be unproved; they attribute the results to possible reaction between the hydrogen bromide and the drying agent employed.

The reaction of hydrogen and bromine has been discussed in considerable detail to show the applicability of the concept of stationary states to the formulation[74] of rate expressions from assumed mechanisms and also to illustrate the manner in which photochemical data may be employed as aids to the solution of other physical chemical problems, as for example, the heat of dissociation of hydrogen or the rates of recombination of bromine atoms. In this way the manner in which photochemical investigations interlock with other phases of physical chemistry becomes apparent.

REACTIONS OF INTERHALOGEN COMPOUNDS

Mellor and Iredale[75] find hydrogen and iodine chloride to react rapidly in strong light if the hydrogen pressure is large compared with that of the iodine chloride, indicating that this condition favors the reaction $H_2 + Cl \rightarrow HCl + H$ so that excited chlorine atoms may not be required for reaction. In thin glass bulbs a reaction between hydrogen and iodine chloride occurs very slowly in artificial light, more rapidly in diffuse daylight and very rapidly in direct sunlight. The products are chiefly iodine and hydrogen chloride. They later state that the reaction can be brought about with pressures of hydrogen comparable with that of the iodine chloride.[76] Methane also reacts rapidly with iodine chloride in light.[77]

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[71] See also Urmston, J., and Badger, R. M., *J. Am. Chem. Soc.* **56**, 343 (1934).

[72] Armour, R. W., and Ludlam, E. B., *Proc. Roy. Soc Edinburgh*, **49**, 91 (1929), *Chem Abs.*, **23**, 3856 (1929).

[73] Bodenstein, M., and Jost, W., *J. Am. Chem. Soc.*, **49**, 1416 (1927).

[74] For a discussion of the validity of the method, see Bodenstein, M., *Trans. Faraday Soc.*, **27**, 409 (1931).

[75] Mellor, D. P., and Iredale, T., *Nature*, **127**, 93 (1931).

[76] *Cf.* Rollefson, G K., and Lindquist, F. E., *J. Am. Chem. Soc.*, **53**, 1184 (1931).

[77] Ashley, S., and West, W., *Nature*, **127**, 308 (1931)

Chapter 18

The Hydrogen-Chlorine Combination

Although apparently one of the simplest photochemical changes, this reaction has been for over a century the subject of an extraordinary amount of investigation because actually it has offered extreme difficulties in both experimental observation and in interpretation. The experimental results have frequently been in disagreement, largely because small quantities of impurities exert such a remarkable effect upon the reaction that reproducible results are difficult to secure. Oxygen, which can be removed from chlorine only with great difficulty, has an inhibiting effect, difficult to eliminate. Other impurities, entirely unsuspected, have been responsible for an inert period after the start of illumination before the reaction begins to build up to its maximum rate. Since studies on this reaction were among the first quantitative photochemical investigations, the finding of this induction period was for a time assumed to be a general photochemical phenomenon, an error which greatly affected the early development of photochemical theory. A thorough review of the history of this reaction would fill many pages. Since excellent summaries are available[1] and since most of the data are concerned with the effects of visible rather than ultraviolet light, the account in this chapter will be limited to a consideration of certain of the more significant features of the work on the reaction, following a statement of the viewpoint at present most generally held in regard to the mechanism.

SPECTRAL ABSORPTION DATA

1. **Hydrogen Chloride.** The absorption of hydrogen chloride consists only of four continuous bands in the short-wave region (2150-1850, 1750-1650, 1580-1290 and 1270-1240A). The absorption spectra of the halide apparently has no significance for the course of the reaction involving hydrogen and chlorine.[2] When irradiated in its absorption region, hydrogen chloride dissociates into a normal hydrogen and an excited chlorine atom, Trivedi[3] finding from the absorption spectrum a heat of dissociation equivalent to 103.9 kcal. Coehn and Wassiljewa[4] and Berthelot and Gaudechon[5] observed slight decomposition to occur as a result of irradiating hydrogen chloride in this wave-length region. According to Schultz[6] not more than 5 molecules may be decomposed per quantum absorbed.

2. **Absorption of Chlorine.** Chlorine absorbs in two broad regions. The first, to which the gas owes its color, extends from about 6430A (or possibly

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[1] Griffith, R. O., and McKeown, A., "Photo-Processes in Gaseous and Liquid Systems," London, Longmans, Green and Co., 1929, Chapter X; Bodenstein, M., *Trans. Faraday Soc.*, **27**, 413 (1931); Thon, N., *Fortschritt Chem. Physik, physik. Chem.*, **18**, No. 11 (1926); Marshall, A. L., *Trans. Am. Electrochem. Soc.*, **49**, 143 (1926).

[2] Leifson, S., *Astrophys. J.*, **63**, 73 (1926).

[3] Trivedi, H., *Proc. Natl. Acad. Sci. India*, **6**, 18 (1936); *Chem. Abs.*, **30**, 4759 (1936).

[4] Coehn, A., and Wassiljewa, A., *Ber.*, **42**, 3183 (1909).

[5] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **156**, 889 (1913).

[6] Schultz, C. T., *J. chim. phys.*, **26**, 506 (1929); *Brit. Chem. Abs.* **A**, 173 (1930).

longer) to about 2500A. Its maximum lies at about 3340A. Extinction values have been given by v. Halban and Siedentopf.[7] There is a minimum in the yellow and the absorption then increases toward longer wave-lengths to a maximum which probably lies between 6140 and 6430A. The spectrum at longer wave-lengths is banded, the absorption coefficients of the bands having very low values.[8] The edges of the bands converge to a limit at 4785A, the absorption being continuous at shorter wave-lengths.[9] It is only in the continuous region that the absorption coefficients attain large values. Here the molecule is dissociated into one normal chlorine atom and one bearing an energy of excitation of 0.109 volt.[10] Since the maximum absorption occurs at a wave-length much shorter than the convergence limit, the excess energy of the light must appear as large amounts of kinetic energy possessed by the dissociated atoms.

The second absorption region extends from about 1900 to 1560A and is entirely continuous.[11] It corresponds to a dissociation similar to that produced by absorption in the region of longer wave-lengths, except that the atoms produced are endowed with greater kinetic energies. From these considerations it is evident that the primary process in the hydrogen-chlorine combination must consist in the formation of chlorine atoms when the mixture of gases is irradiated with wave-lengths shorter than 4785A.

To account for various features of the photochemical reaction anomalies of absorption have been assumed. Statements that the absorption by chlorine is dependent upon the intensity of the incident light[12] could not be confirmed by Gray and Style.[13] For a long period water was believed necessary for the photochemical reaction between hydrogen and chlorine. It was stated that the disposition of energy absorbed by moist and by dry samples of chlorine is different.[14] No difference in absorption was observed by v. Halban and Siedentopf, Kistiakowsky[15] or Kornfeld and Steiner.[16] Furthermore, no fluorescence could be detected within the continuous region.

Budde Effect. A phenomenon which excited considerable interest and which at one time appeared important for the explanation of the mechanism of the hydrogen-chlorine combination was the observation by Budde[17] that chlorine gas expands when illuminated by white or blue light but not when red or yellow light is employed. He found the expansion the result of a temperature increase, an observation confirmed by Bevan.[18] Richardson[19] found the expansion to be roughly proportional to the intensity of the light employed. The effect is usually attributed to heat liberated as a result of the recombination of chlorine atoms formed by the absorption within the continuous region. The effects of small amounts of moisture on the extent of this effect have been discussed since the observations of Shenstone,[20] who found pure dry chlorine to give only a very small Budde effect. This effect could be increased by the admission of some moisture.[21]

[7] v. Halban, H., and Siedentopf, K., *Z. physik. Chem.*, **103**, 71 (1922).
[8] Kuhn, H., *Z. Physik*, **39**, 77 (1926).
[9] Elliott, A., *Proc. Roy. Soc.* **123**, 629 (1929); **127**, 638 (1930).
[10] Birge, R. T., *Phys. Rev.*, **35**, 133 (1930).
[11] Cordes, H., and Sponer, H., *Z. Physik*, **63**, 334 (1930).
[12] Weigert, F., and Brodmann, L., *Z. physik. Chem.*, **106**, 426 (1923).
[13] Gray, L. T. M., and Style, D. W. G., *Proc. Roy. Soc.* **126A**, 603 (1930).
[14] Mellor, J. W., *J. Chem Soc*, **81**, 1280 (1902).
[15] Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **49**, 2194 (1927).
[16] Kornfeld, G., and Steiner, W., *Z. Physik*, **45**, 325 (1927).
[17] Budde, E., *J. prakt. Chem.*, **7**, 376 (1873).
[18] Bevan, P. V., *Phil. Trans.*, **202**, 90 (1904).
[19] Richardson, A., *Phil. Mag.*, **32**, 221, 277 (1891).
[20] Shenstone, W. A., *J. Chem. Soc.*, **71**, 471 (1897).
[21] See also Ludlam, E. B., *Proc. Roy. Soc. Edinburgh*, **34**, 197 (1924).

Kistiakowsky[22] attributed the water dependence of the effect to the necessity for inert molecules to carry off the energy of recombination of chlorine in three-body collisions. In the absence of water, the free chlorine atoms could combine only on the glass walls of the vessel. The large heat capacity and relatively good heat conductance of the vessel would, however, prevent the heating of the gas and so the Budde effect would be missed. On the other hand, Martin, Cole and Lent[23] and more recently, Kiastiakowsky[24] have denied the effect of drying in lessening the photoexpansion of chlorine. Narayana,[25] however, states that the Budde effect cannot be observed in dry gases, unless the vessel is carefully vacuum-insulated. In accordance with the theory that a primary dissociation is essential, the effect is absent in chlorine illuminated by wave-lengths greater than 5000A and in bromine above 5500A. It varies as the pressure of the halogen and as the square root of the intensity of the light.

In the case of bromine, Lewis and Rideal[26] have advanced evidence in support of a different mechanism. They believed a bromine-hydrate (heat of formation 1.09 kcal.) to be dissociable by wave-lengths 5700-5400A, in the band rather than in the dissociation region of the spectrum. Thus the bromine hydrate could be dissociated by wave-lengths longer than those required for the dissociation of dry bromine. Recombination of the bromine and water was held to give rise to the heat which produces the characteristic expansion. Matthews[27] has found drying to lessen somewhat the Budde effect, although it could not be entirely eliminated in this manner.

MECHANISM OF THE HYDROGEN-CHLORINE COMBINATION

The outstanding characteristic of the hydrogen-chlorine combination is the high quantum yield. Bodenstein[28] calculated that, were it possible to eliminate traces of inhibiting oxygen from the chlorine employed, the yield should be approximately 10^6. Kornfeld and Müller[29] found it to be 1.10×10^5 for light of 4360A. Harris[30] has, by using blue light and very carefully purified gases, obtained a value of 6×10^5 and Bodenstein and Winter[31] of 4.2×10^6 in silver vessels. This corresponds to an average chain duration of 16 seconds. Obviously, such quantum yields require a chain mechanism and many have been proposed. At this point, mention of the mechanism which apparently is most favored, will be made and discussion of the effects of inhibitors will be postponed until the experimental data have been discussed. The primary process is a photodissociation of the chlorine into atoms. The subsequent reactions which form the chain were first suggested by Nernst.[32]

$$\begin{aligned}
&(1)\quad Cl_2 + h\nu(< 4785\text{A}) \longrightarrow Cl + Cl\\
&(2)\quad Cl + H_2 \longrightarrow HCl + H\\
&(3)\quad H + Cl_2 \longrightarrow HCl + Cl
\end{aligned}$$

Rodebush and Klingelhöfer[33] have advanced more cogent evidence than that originally suggested by Nernst for the thermodynamic possibility of reaction (2), although they believe that only every 10^5th collision leads to reaction. The activation energy is 6.1 kcal. Marshall[34] calculated for reaction (2) a free energy change of approximately zero. Reaction (3) is believed by Bodenstein to occur at each hundredth collision. Since it regenerates a free chlorine atom, the chain mechanism would be readily apparent did reaction (2) occur.

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[22] Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **49**, 2199 (1927).

[23] Martin, W. H., Cole, A. F. W., and Lent, E. E., *J. Phys. Chem.*, **33**, 148 (1929).

[24] Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **51**, 1395 (1929).

[25] Narayana, T. S., *Indian J. Physics*, **9**, 91 (1934); *Chem. Abs.*, **29**, 684 (1935).

[26] Lewis, B., and Rideal, E. K., *J. Chem. Soc.*, 583, 596 (1926).

[27] Matthews, E., *Trans. Faraday Soc.*, **25**, 41 (1929); *cf.* Ritchie, M., and Ludlam, E. B., *J. Chem. Soc.*, 1680 (1937).

[28] Bodenstein, M., *Z. physik. Chem.*, **85**, 351 (1913).

[29] Kornfeld, G., and Müller, H., *Z. physik. Chem.*, **117**, 242 (1925).

[30] Harris, L., *Proc. Nat. Acad. Sci.*, **14**, 110 (1928).

[31] Bodenstein, M., and Winter, E., *Sitzber. preuss. Akad. Wiss., Physik-math. Kl.*, 2 (1936).

[32] Nernst, W., *Z. Elektrochem.*, **24**, 335 (1918).

[33] Rodebush, W. H., and Klingelhöfer, W. C., Jr., *Proc. Nat. Acad. Sci.*, **18**, 531 (1932); *J. Am. Chem. Soc.*, **55**, 130 (1933).

[34] Marshall, A. L., *J. Phys. Chem.*, **29**, 842 (1925).

Many efforts were made to demonstrate experimentally the occurrence of reaction (2), including the work of Jost and Schweitzer.[35] Could this reaction be admitted, it is apparent that the great difference between the hydrogen-bromine and the hydrogen-chlorine combinations would be readily explicable. The failure of many direct attempts to show experimental proof for reaction (2), however, delayed for several years the acceptance of the simple Nernst chain mechanism and led to the proposal of a number of alternative mechanisms which attempted to avoid the use of this reaction. Included among these proposals were the presence of excited chlorine molecule chains or of chains carried by excited HCl or by a postulated triatomic chlorine molecule.

Attempts to activate chlorine by a brush electric discharge or by a mercury lamp so that when conducted into unilluminated hydrogen the two substances would produce hydrogen chloride were made (unsuccessfully) by Wendt.[36] Other unsuccessful attempts were described by Bodenstein and Taylor[37] and by Marshall.[38] Jost and Schweitzer were able to demonstrate the reaction (2) by passing a very rapid stream of irradiated chlorine into hydrogen. The free atoms, however, recombine rapidly on the walls of the conducting tube and the experiment fails when the irradiated gas remains in the tube longer than 10^{-4} second. Nevertheless, with the demonstration of the possibility of the reaction, the Nernst chain becomes admissible. It is thus conceivable that there can be a long-continued interplay of reactions (2) and (3) leading to the production of large numbers of molecules of hydrogen chloride consequent upon the absorption of one quantum of light, before the free atoms which carry the chains are lost by wall reactions or by interactions with impurities, *e.g.*, oxygen.

History of the Work on the Reaction. That a mixture of hydrogen and chlorine explodes in bright sunlight and reacts slowly in diffused light was first observed by Cruikshank.[39] Quantitative rate measurements, the first on any photochemical change, were made by Draper[40] by means of a "tithonometer." In this apparatus the hydrogen chloride produced was absorbed in water, and the volume contraction was followed by the movement of a column of liquid along a capillary. Draper found indigo rays the most powerful in causing the contraction, as did Favre and Silbermann.[41]

In the course of this work what has come to be known as the Draper effect[42] was discovered. This consists of a brief expansion on exposure to light, followed by a period in which there is no pressure change, and then by a contraction. The details of the Draper effect were studied by Mellor and Anderson,[43] Bevan,[44] and by Weigert and Kellerman.[45] Bevan, who could produce the Draper effect only by use of fairly intense light, attributed the effect to a rise of temperature accompanying the formation of hydrogen chloride. Weigert made a detailed study of the time relations involved, employing a photographic Töpler cloud method depending upon local changes of refractive index. The magnitude of the effect was related to the degree of drying of the gases. The cloud observed when a mixture of chlorine and electrolytic gas was irradiated with light of short wave-length paralleled the Draper effect in time-intensity relations. The cloud was assumed due to a warming of the gas and the amount of thermal expansion corresponded with the calculated amount of heat which is liberated during the production of the hydrogen chloride. Weigert's theory of clustering about a group of two molecules between which an electron has passed from the hydrogen molecule to the chlorine molecule did not prove significant. His experimental observation that the change in density did not begin until 10^{-4} second after irradiation by a single spark discharge and attained its maximum only some hundredths of a second after the irradiation gave direct evidence for the existence of a chain reaction.

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[35] Jost, W., and Schweitzer, H., *Z. physik. Chem.*, **13B**, 373 (1931).

[36] Wendt, G. L., *Chem. Met. Eng.*, **24**, 83 (1921); Wendt, G. L., Landauer, R. S., and Ewing, W. W., *J. Am. Chem. Soc.*, **44**, 2377 (1922). See, however, Venkataramaiah, Y., *J. Phys. Chem.*, **27**, 74 (1923).

[37] Bodenstein, M., and Taylor, H. S., *Z. Elektrochem.*, **22**, 202 (1916).

[38] Marshall, A. L., *J. Phys. Chem.*, **30**, 757 (1926).

[39] Cruikshank, W., *Nicholson's J.*, **5**, 202 (1801).

[40] Draper, J., *Phil. Mag.*, **19**, 195 (1841); **23**, 40 (1843); **25**, 237 (1844).

[41] Favre, P. A., and Silbermann, J. T., *Ann. chim. phys.*, **37**, 497 (1853). Allmand, A. J., and Beesley, E. [*J. Chem. Soc.*, 2694, 2709 (1930); 157 (1934)] find the violet region the most effective.

[42] Draper, J., *Phil. Mag.*, **26**, 476 (1845).

[43] Mellor, J. W., and Anderson, W. R., *J. Chem. Soc.*, **81**, 414 (1902).

[44] Bevan, P. V., *Phil. Trans.*, **202**, 81 (1904).

[45] Weigert, F., and Kellerman, K., *Z. physik. Chem.*, **107**, 1 (1924).

Induction Period. Bunsen and Roscoe made studies of the rate of the reaction; an improved "actinometer" was used for correlating the reaction rate and the light intensity.[46] In the course of this work they described in detail an earlier observed induction period to which they ascribed unwarranted *general* photochemical significance. The details given by them and by later workers[47] were confusing and indicated the induction period to be dependent on the length of the gas column irradiated, the intensity of the light, the temperature and the previous history of the gas. The interpretation of the results was further complicated by the belief of Bunsen and Roscoe that the absorption of the gases during reaction is increased over that of unreacting gases, a view now known to have been erroneous. The simple explanation that the induction period is due to the presence of small amounts of inhibiting impurities which are destroyed in large part during the inert period was established by Burgess and Chapman.[48] They found no difference in the extinction of irradiated and non irradiated gas mixtures. Also, oxygen did not affect the length of the induction period, and traces of ammonia could produce very long induction periods, the duration of which varied directly as the concentration of the added ammonia. A later suggestion by Chapman and McMahon[49] that the inhibition should be attributed to the production of NCl_3 by the interaction of chlorine with the ammonia was, however, considered untenable by Norrish.[50] Norrish advanced the view that the ammonia derived from the impurities was adsorbed on the surface of the vessel, poisoning the latter for certain surface reactions involving a water-chlorine compound. Arguments were raised against this theory by Cathala[51] Griffiths and Norrish[52] have accepted the view that the induction period is due to the formation of NCl_3, which undergoes photosensitized decomposition in the presence of excess chlorine by short reaction chains. The quantum efficiency of this reaction falls to about two as the chlorine pressure is increased.

Nitric oxide (but not nitrous oxide) and chlorine dioxide also inhibit the reaction.[53] Oxygen apparently slows the rate of the reaction rather than causes an induction period. The effect of oxygen in inhibiting the reaction is not attended by its total disappearance, as is that of the inhibitors responsible for the induction period. The rate of the formation of hydrogen chloride has been found to be inversely proportional to the oxygen concentration, at least over the range, 0.09 to 1.00 per cent.[54]

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[46] Bunsen, R., and Roscoe, H., *Pogg Ann*, **96**, 373 (1855); **100**, 193 483 (1857); **101**, 32, 237, 275 (1857); **108**, 193 (1859), **117**, 531 (1862); Reprinted in *Ostwald's Klassiker*, No. 34 and 38 (1892).

[47] Pringsheim, E., *Wied. Ann*, **32**, 384 (1887); Mellor, J. W, *J. Chem. Soc.*, **81**, 1292 (1902).

[48] Burgess, C. H., and Chapman, D. L., *J. Chem. Soc.*, **89**, 1399 (1906).

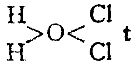
[49] Chapman, D. L., and McMahon, P. S., *J. Chem. Soc.*, **95**, 1717 (1909); **97**, 847 (1910).

[50] Norrish, R. G. W., *J. Chem Soc.*, **127**, 2316 (1925).

[51] Cathala, J., *Bull. Soc. Chim.*, **39**, 612 (1926).

[52] Griffiths, J. G. A., and Norrish, R. G. W, *Trans. Faraday Soc.*, **27**, 451 (1931); *Proc. Roy. Soc.*, **147A**, 140 (1934)

[53] Chapman, D. L, and McMahon, P. S., *J. Chem. Soc.*, **95**, 959 (1909).

Effects of Water Vapor. From the earliest to the most recent studies, attention has been directed to the effects of traces of water vapor on the hydrogen-chlorine combination. Baker[55] claimed that under conditions of extreme dryness, the reaction proceeds only very slowly in direct sunlight, but Mellor and Russell[56] found that even these extremely dry mixtures could be made to explode by an electric spark. Bodenstein and Dux[57] found the rate of combination of the gases to be unaffected by drying down to a water vapor pressure of 10^{-3} mm. of mercury. Tramm,[58] however, found that drying by a special liquid air technique prevented the combination from occurring in sunlight. Coehn and Jung[59] claimed that the photochemical reaction was prevented when the water vapor pressure was reduced below 10^{-7} mm. and visible light was the source employed. When the effective light was of wave-length shorter than about 2540A the reaction was not prevented by drying, although the quantum yield was lowered to about eight. On the basis of these results, Norrish[60] advanced the theory that water is required as a catalyst in the primary process. He believed an intermediate compound  ${}^{H}_{H}\!>\!O\!<\!{}^{Cl}_{Cl}$ to be formed and adsorbed on the walls of the vessel where subsequent reaction occurs. Coehn's explanation of the effect of water (an effect due to water in atomic chlorine reactions) appeared inadequate both to Norrish and to Cathala.[61] The latter worker, however,[62] was unable to accept the theory of Norrish. Kistiakowsky,[63] pointed out that the theory of Norrish had been disproved by the experiments of Coehn and Heymer[64] in which a chlorine and hydrogen mixture reacted on exposure to radiation in apparatus arranged to minimize solid and liquid surfaces. For a time it was believed that water might be required to enable the absorption of radiation by chlorine leading to dissociation of the latter into atoms.[65]

As the spectroscopic evidence on the dissociation process gained prominence, it became necessary to discard such views. The effect of water vapor was next attributed to some possible influence exerted by it on the rate of recombination of free chlorine atoms.[66] Recently, however, in view of the inadequacy of the explanations which could be advanced to explain the mechanism by which water vapor aids the reaction, the tendency has been to reëxamine the validity of the phenomenon. Particularly is this necessary, since it would be very difficult to explain why water vapor should have a greater effect upon chlorine atoms produced by visible radiations than by shorter rays as had been claimed by Coehn and Tramm. Bodenstein and Bernreuther[67] suggest that the earlier observations may have been due to the accidental introduction of strong inhibitors such as metal chlorides in the drying methods employed. The work of Rollefson and Potts[68] indicates that at low temperatures at least, the presence of water vapor has no marked effect on the rate of the reaction.

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[54] Bodenstein, M., and Dux, W., *Z. physik. Chem.*, **85**, 297 (1913).

[55] Baker, H. B., *J. Chem. Soc.*, **65**, 612 (1894).

[56] Mellor, J. W., and Russell, E. J., *J. Chem. Soc.*, **81**, 1272 (1902)

[57] Bodenstein, M., and Dux, W., *Z. physik. Chem*, **85**, 297 (1913).

[58] Tramm, H., *Z. physik. Chem.*, **105**, 356 (1923).

[59] Coehn, A., and Jung, G., *Ber.*, **56**, 696 (1923).

[60] Norrish, R. G. W., *J. Chem. Soc.*, **127**, 2316 (1925); *Trans Faraday Soc*, **21**, 575 (1925).

[61] Cathala, J., *Compt. rend.*, **181**, 33 (1925).

[62] Cathala, J., *Bull. Soc. Chim.*, **39**, 612 (1926).

[63] Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **49**, 2194 (1927).

[64] Coehn, A., and Heymer, G., *Naturwiss.*, **14**, 299 (1926); *Ber.*, **59B**, 1794 (1926).

[65] Lewis, B., *Nature*, **120**, 473 (1927); Weigert, F., *Z. physik. Chem.*, **106**, 426 (1923). Ichikawa, T., *Z. physik. Chem.*, **10B**, 299 (1930).

[66] Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **49**, 2194 (1927).

Development of Chain Mechanisms. The first chain mechanism suggested by Bodenstein involved an ionized chlorine molecule[69] but this was soon shown to be excluded[70] by the observations that no ionization occurs in irradiated chlorine gas,[71] or during the photocombination of hydrogen and chlorine.[72] Bodenstein[73] next proposed a mechanism in which the chains were assumed to be carried both by activated chlorine and activated hydrogen chloride molecules, a view supported in principle (although not in the details of chain propagation) by Stern and Volmer.[74]

The dissociation theory of Nernst[75] was proposed in 1918; many attempts followed to decide between the "hot molecule" and the dissociation theories. Attempts to compare rates and quantum yields of light and α-ray induced reactions[76] failed to afford a basis for a decision. Much labor was devoted to efforts to settle the question by kinetic studies. The earlier attempts were also equivocal, and it became evident that with sufficient ingenuity the kinetic data obtained under various experimental conditions might be interpreted with some degree of success by employing the concepts of either theory. The details of the many proposed mechanisms, some of which involved as many as eleven reaction constants (for the most part undetermined or undeterminable) cannot be given here.

REACTION KINETICS[76a]

Contrary to Baly and Barker,[77] more recent observers find the rate of the formation of hydrogen chloride proportional to the light intensity.[78] Rollefson found the rate of formation also proportional to the hydrogen and chlorine[79] concentrations. He reasoned that if the reaction were due to excited molecules, the velocity constant should decrease rapidly at low pressures, since the time between collisions would then be long enough to permit the excitation energy to be lost by fluorescence. Should the reaction be due to free atoms, the rate constant should be independent of the pressure. From kinetic considerations and from the probable life of an excited chlorine molecule, he calculated that it should be possible to distinguish between these mechanisms at a hydrogen pressure of one millimeter. His data showed no change in the rate constant as the pressure was decreased below this limit and therefore afforded support for the dissociation mechanism.

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[67] Bodenstein, M., and Bernreuther, F., *Berl. Preuss. Akad. Wiss., Phys. math. Klasse*, 333 (1933); *Chem. Abs.*, **27**, 3669 (1933).

[68] Rollefson, G. K., and Potts, J. C., *J. Am. Chem. Soc.*, **55**, 860 (1933).

[69] Bodenstein, M., *Z. physik. Chem.*, **85**, 329 (1913).

[70] LeBlanc, M., and Volmer, M., *Z. Elektrochem.*, **20**, 494 (1914).

[71] Ludlam, E. B., *Phil. Mag.*, **23**, 757 (1912).

[72] Thomson, J. J., *Proc. Cambr. Phil. Soc.*, **11**, 901 (1901).

[73] Bodenstein, M., *Z. Elektrochem.*, **22**, 53 (1916).

[74] Stern, O., and Volmer, M., *Z. wiss. Phot.*, **19**, 275 (1920).

[75] Nernst, W., *Z. Elektrochem.*, **24**, 335 (1918).

[76] Bodenstein, M., *Z. Elektrochem.*, **22**, 53 (1916); Taylor, H. S., *J. Am. Chem. Soc.*, **37**, 24 (1915); **38**, 280 (1916). Porter, F., Bardwell, D. C., and Lind, S. C., *J. Am. Chem. Soc.*, **48**, 2603 (1926).

[76a] For the evaluation of the various rate constants, see Taylor, H. S., *J. Phys. Chem.*, **42**, 789 1453

[77] Baly, E. C. C., and Barker, W. F., *J. Chem. Soc.*, **119**, 653 (1921).

[78] Chapman, M. C. C., *J. Chem. Soc.*, **125**, 1521 (1924); Marshall, A. L., *J. Phys. Chem.*, **29**, 1453 (1925); Allmand, A. J., and Beesley, E., *J. Chem. Soc.*, 2693 (1930). Rollefson, G. K., *J. Am. Chem. Soc.*, **51**, 770 (1929); Bateman, J. B., and Craggs, H. C., *Trans. Faraday Soc.*, **27**, 445 (1931); Bodenstein, M., and Unger, W., *Z. physik. Chem.*, **11B**, 253 (1930); see, however, Squire, G. V. V., and Allmand, A. J., *J. Chem. Soc.*, 1869 (1937).

[79] See, however, Bodenstein, M., and Dux, W., *Z. physik. Chem.*, **85**, 297 (1913); Thon, N., *Z. physik. Chem.*, **124**, 327 (1926). For the influence of oxygen on the rate, see Chapman, M. C. C., *loc. cit.*; Norrish, R. G. W., and Rideal, E. K., *J. Chem. Soc.*, **127**, 787 (1925).

Recently efforts have been directed toward an understanding of the manner in which, in pure gases, the chains are broken by the removal of the atoms. Reactions at the wall were suggested by Chapman and Grigg[80] for destroying the catalyst (the nature of which then was not considered) since the reaction was slower in capillary tubes than when conducted under the same light intensity in tubes of wider bore. Trifonoff,[81] who suggested that grease on the stopcocks might start the reaction, believed that recombination of atoms diffused to the walls at low pressures might break the chains. At pressures above 30 mm., he believed the processes to occur chiefly in the free space, but below 10 mm. practically all of the chains break down at the surfaces of the walls. Bodenstein and Unger were also of the opinion that at higher pressures the chains must be broken by some compound present in the reaction space. A volatile deposit, possibly of a silicon oxychloride, has been detected on the walls of vessels in which free chlorine atoms had been produced. Hertel[82] thought that this might be responsible for breaking the chains, since the rate of formation of hydrogen chloride could be lowered by carrying out the reaction in vessels in which chlorine had previously been irradiated. He had found that the rate[83] might be expressed by $k_1(H_2)(Cl_2)^2$ when the chlorine is present in great excess and by $k_2(H_2)^2(Cl_2)$ when the hydrogen is in great excess. He also gave a more general equation, which need not be reproduced here. Hertel believed that the observed rate could be accounted for on the assumption that oxygen terminates the chains by combining with the hydrogen atoms. Chapman and Gibbs[84] find the rate of the reaction proportional to the square root of the intensity of the light when the chlorine used has been very carefully freed from oxygen and other inhibiting impurities.

Behavior at very low pressures similar to that found by Rollefson has also been reported by Allmand and Craggs,[85] the reaction proceeding at the normal rate even at chlorine pressures as low as 0.012 mm. Water vapor also failed to affect the rate except at low total pressures. They stated that at total pressures of 2 mm. ultraviolet light affords lower quantum yields than does visible light, but this difference is not observed at higher pressures. It was thought that it might be accounted for by the formation of triatomic chlorine molecules by the ultraviolet of short wave-length. By quantum mechanical considerations, Rollefson and Eyring[86] concluded that, for all the halogens, molecules of the type X_3 are stable at room temperatures with respect to dissociation into X_2 and X. Cremer[87] had previously suggested the possibility that this molecule might function as a chain carrier, as had Cathala[88] who called it "chlorozone."[89]

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[80] Chapman, D. L., and Grigg, P. P., *J. Chem. Soc.*, 3233 (1928).

[81] Trifonoff, A., *Z. physik. Chem.*, **3B**, 195 (1929); **6B**, 118 (1929); Trifonoff, A., and Ryabinin, G., *Trans. State Phys.-Tech. Lab. (Moscow)*, No. **14**, 26 (1930); *Chem. Abs.*, **24**, 1297 (1930).

[82] Hertel, E., *Z. physik. Chem.*, **15**, 325 (1932).

[83] Hertel, E., *Z. physik. Chem.*, **14B**, 443 (1931).

[84] Chapman, D. L., and Gibbs, F. B., *Nature*, **127**, 854 (1931).

[85] Allmand, A. J., and Craggs, H. C., *Nature*, **130**, 927 (1932); *J. Chem. Soc.*, 241 (1936); 1889 (1937). Craggs, H. C., Squire, G. V. V., and Allmand, A. J., *J. Chem. Soc.*, 1878 (1937).

[86] Rollefson, G. K., and Eyring, H., *J. Am. Chem. Soc.*, **54**, 170 (1932).

[87] Cremer, E., *Z. physik. Chem.*, **128**, 285 (1927).

[88] Cathala, J., *J. chim. Phys.*, **25**, 182 (1928).

[89] For further discussion of chain carriers for this reaction see Göhring, R., *Z. Elektrochem.*, **27**, 516 (1921); Chapman, D. L., *Trans. Faraday Soc.*, **21**, 547 (1925) and Warburg, E., *Z. Elektrochem.*, **27**, 139 (1921).

[90] Bodenstein, M., and Schenk, P. W., *Z. physik. Chem.*, **20B**, 420 (1933).

Allmand and Craggs state that the presence of 0.1 mm. of oxygen retards the reaction between chlorine and less than 0.01 mm. of hydrogen. It has no effect, however, when there is 0.01 to 0.5 mm. of hydrogen, but under these conditions the oxygen is consumed.

Results of Bodenstein and Schenk[90] on the relative yields of hydrogen chloride and of water in streaming mixtures of chlorine, hydrogen and oxygen at 60°C. have been criticized by Chapman and Watkins,[91] who employed mixtures rich in oxygen. Ritchie and Norrish,[92] who determined the reaction rate by measuring the chlorine absorption, found hydrogen chloride to have a pronounced inhibiting effect on mixtures which contained oxygen. In the absence of oxygen, the quantum efficiency is given by the expression

$$\frac{2.8 \times 10^{6}(\mathrm{H_2})(\mathrm{Cl_2})}{(\mathrm{Cl_2})+1.7(\mathrm{HCl})(\mathrm{I_{Abs}})^{0.4}}.$$

Their maximum quantum yield was 1.2×10^5. The velocity of hydrogen chloride formation varies with the 0.6 power of the intensity of the absorbed light in approximate agreement with Chapman and Gibbs. Reaction chains are terminated mainly by self-neutralization.[93] In the presence of oxygen, both hydrogen chloride and hydrogen have inhibiting effects, that of the former being four times that of the latter. With increasing hydrogen pressures, the quantum efficiency rises through a maximum. For mixtures rich in oxygen, it varies inversely as the oxygen pressure and is independent of the light intensity. The quantum efficiency is also reduced by inert gases.[94] At low concentrations of oxygen, it shows a dependence on the light intensity.

According to Krauskopf and Rollefson,[95] as the ratio of oxygen to chlorine is increased, the ratio of the production of water to that of hydrogen chloride approaches a limit between one and two. From its temperature dependence, the activation energy for the reactions yielding hydrogen chloride appears to be greater than that for those yielding water. They hold that the existence of the limit for the ratio of the two products shows that the Nernst chains must be terminated by a reaction $\mathrm{H + O_2 \rightarrow HO_2}$ rather than by $\mathrm{Cl + O_2 \rightarrow ClO_2}$. Rollefson and Potts[96] state that at temperatures below 172°K., the melting point of chlorine, the rate depends on the square root of the light absorbed. From the temperature coefficients, observed at 3600A, the heat of activation is 5.8 kcal. At low temperatures the value 4.6 kcal. is, however, found. They accept the suggestion that a volatile silicon oxychloride terminates the chains. They suggest further that the large inhibiting effect of hydrogen chloride observed by Norrish and Ritchie may have been due to the introduction of an inhibiting impurity in the hydrogen chloride added. The rate equation given by Rollefson and Potts is said to be valid at temperatures as low as 200°K. The equation is:

$$\frac{d(\mathrm{HCl})}{dt} = k\mathrm{I_{Abs}}(\mathrm{H_2})\frac{1}{1+k_1\dfrac{(\mathrm{HCl})}{(\mathrm{Cl_2})}},$$

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[91] Chapman, D L., and Watkins, J. S. *J. Chem. Soc*, 743 (1933)

[92] Ritchie, M., and Norrish, R. G. W., *Proc. Roy. Soc.*, **140**, 99, 112, 713 (1933).

[93] See also Tamura, M., *Rev. Phys. Chem. Japan*, **11**, 1 (1937); *Chem Abs.*, **32**, 1184 (1938).

[94] Ritchie, M., *J. Chem Soc.*, 857 (1937)

[95] Krauskopf, K. B., and Rollefson, G. K., *J. Am. Chem. Soc.*, **56**, 327 (1934); see also Ritchie, M., *J. Chem. Soc.*, 857 (1937).

[96] Rollefson, G. K., and Potts, J. C., *J. Am. Chem. Soc.*, **57**, 1027 (1935).

in which $k_1 \leq 0.1$. Some of the proposed chain mechanisms have been discussed by Bates.[97] An interesting direct method of demonstrating the existence of a chain reaction has been the application of the para-hydrogen test for the presence of free hydrogen atoms,[98] to which reference has been made in a preceding chapter. Kokochashvili[99] has studied the reaction by the aid of very brief irradiations (.08 second) of high intensity secured by magnesium flashes, and has discussed his results from the standpoint of chain mechanisms. Deuterium molecules are less reactive than hydrogen, the activation energy being slightly higher for the former.[100] Farkas and Farkas[101] find the reaction with deuterium to proceed at one-third the rate of that with hydrogen. They ascribe the difference in rates to the larger zero-point energy of hydrogen as compared with deuterium. The calculated additional activation energy of 0.8 kcal. required by deuterium agrees well with the difference in zero-point energy between H^1_2, HD and D_2 of 810 and 1710 cal.

Thresholds and the Effects of Wave-Lengths

Within the continuous region, Bodenstein and Schenk[102] found the quantum yield to be independent of the wave-length. Allmand and Beesley,[103] using filters, gave the following *relative* values: 2600A, 0.10; 3130A, 0.49; 3650A, 0.53; 4050A, 1.00; 4360A, 0.67 and 5460A, 0.22. On the other hand, Bateman and Allmand[104] found the quantum yield independent of the wave-length between 4000A and 4900A, but observed it to fall slowly on either side of this region. The earlier results were attributed to the accidental use of a glass window. A result at 4920A was considered anomalous since the ratio between the yield at this wave-length and that at 4050A rose on prolonged irradiation from an initial value of 0.6 to a constant value of about 8. Between 4000 and 2900A the yield was of constant order of magnitude, but appeared to fall off by about 10-20 per cent in going from the visible toward the shorter wave-lengths.[105] The observation that a definite reaction can take place at 5400-5500A is of interest in view of earlier discussions (Chapter 15) regarding the existence of a threshold wave-length for this reaction.[106]

Hertel assumed the primary process to be the formation of excited chlorine molecules under the influence of light in the band region. A small fraction of these molecules is then dissociated by impact with molecules of either hydrogen, chlorine or of hydrogen chloride. The efficiencies of these molecules in effecting dissociation were found to be in the ratio of 1 : 3 : 0.5. As a result of this dissociation, chains are set up as in the continuous region. The quantum yield in the region between 4850 and 5090A was found to be about half that observed by light in the continuous region. Hertel believed it would be very difficult to determine whether the reaction could proceed at wave-lengths longer than 5000A since the absorption is so low in this region. He noted that Dhar and Bhagwat had found a limiting zone at 6650A, and believed that a slight reaction might occur at 7700A.

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[97] Bates, J. R., *Proc. Nat. Acad. Sci.*, 19, 81 (1933).
[98] Geib, K. H., and Harteck, P., *Z. physik. Chem.*, 15B, 116 (1931).
[99] Kokochashvili, V., *Z. physik. Chem.*, 23B, 431 (1933)
[100] Rollefson, G. K., *J. Chem. Physics*, 2, 144 (1934).
[101] Farkas, L., and Farkas, A., *Naturwiss.*, 22, 218 (1934).
[102] Bodenstein, M., and Schenk, P. W., *Z. physik. Chem.*, 20B, 420 (1933).
[103] Allmand, A. J., and Beesley, E., *J. Chem. Soc.*, 2693, 2709 (1930).
[104] Bateman, J. B., and Allmand, A. J., *J. Chem. Soc.*, 157 (1934).
[105] See also Norrish, R. G. W., and Ritchie, M., *Proc. Roy. Soc.*, 140, 99, 112, 713 (1933)
[106] Hertel, E., *Z. physik. Chem.*, 14, 443; 15, 325 (1932).

Recently Allmand and Craggs[107] have found it possible to form hydrogen chloride when mixtures of 0.1-0.6 mm. of hydrogen and 1.7 to 166 mm. of chlorine are irradiated with light of 5460A, a slightly longer wave-length than corresponds to the dissociation of chlorine into normal atoms. It would be expected that if excited molecules are formed and dissociated on impact with other molecules the absorbed energy of excitation must supply most of the energy for the subsequent dissociation. The slight deficiency involved when 5460A is used can, however, be supplied otherwise. If the chlorine molecules which absorb this energy are initially in high vibrational levels they can acquire sufficient energy by the absorption of this wave-length. The results could, it was believed, be correlated with the continuous background of the banded absorption spectrum of chlorine. No reaction occurred at 5790A. From the temperature coefficient of the reaction at 5460A, the activation energy appeared to be 9.78 kcal. The quantum efficiency relative to unity at 4360A was approximately 0.3. Subsequent to a more recent interpretation of the continuous absorption spectrum of chlorine, Bayliss has shown that at all wave-lengths the primary process is the same—dissociation—and that the quantum yield, temperature coefficient and activation energy are independent of the wave-length of the exciting radiation.[108]

In addition to the investigations in which temperature coefficients have been determined for calculations of activation energies, there have been a few earlier observations of temperature coefficients to which very brief reference may be made. Padoa and Butironi[109] seem to have been the first to make such determinations. They found the acceleration produced by increase in temperature to be but small in the ultraviolet, greater for violet and blue light and a maximum for green light. The values were: green (5500-5300A), 1.50; blue (4900-4700A), 1.31; violet (4600-4400A), 1.21; ultraviolet (4000-3500A), 1.17. Hertel's observations gave 1.48 in the band region in good agreement with those of Padoa. The values obtained by Livingston and Lind[110] were somewhat lower.

Lavrov[111] has made many determinations of the critical pressures at which the carbon arc will ignite various mixtures of chlorine, hydrogen and various gases.

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[107] Allmand, A. J., and Craggs, H. C., *J. Chem. Soc.*, 241 (1936).

[108] Aickin, R. G., and Bayliss, N. S., *Trans. Faraday Soc.*, 33, 1333 (1937); Bayliss, N. S., *Ibid.*, 33, 1339 (1937).

[109] Padoa, M., and Butironi, C., *Atti accad. Lincei*, 24 (II), 215 (1916); *Chem. Abs.*, 11, 1356 (1917).

[110] Livingston, R., and Lind, S. C., *J. Am. Chem. Soc.*, 52, 593 (1930).

[111] Lavrov, F. A., and Zagulin, A. V., *Acta Physicochim. U.R.S.S.*, 1, 979 (1934); *Brit. Chem. Abs.*, A, 943 (1936); Lavrov, F. A., and Perel'man, T., *Acta Physicochim. U.R.S.S.*, 2, 91 (1935); *Chem. Abs.*, 29, 6506 (1935).

Chapter 19

Reactions of Inorganic Gases Other than Halogen Halides

REACTIONS OF OXYGEN

The Oxygen-Ozone Transformation. Schönbein, who was the discoverer of ozone, reported that oxygen can be photochemically activated[1] and Nernst[2] interpreted the formation of ozone by the silent electric discharge as a photochemical reaction. Lenard[3] observed formation of ozone in air by the action of sparks from a Leyden jar and demonstrated that it was due to light of wave-lengths less than 2000A. Goldstein[4] succeeded in preparing a dark blue liquid containing a high percentage of ozone within a discharge tube containing oxygen and immersed in liquid air.

With the advent of quartz mercury arcs, reports began to appear regarding the conditions under which a considerable yield of ozone could be produced in air by ultraviolet radiations. Fischer and Braehmer[5] described an apparatus in which electrolytic gas was conducted through an annular narrow space surrounding a quartz-contained mercury arc, the entire apparatus being cooled by immersion in water. Their measurements of the yield of ozone produced under different conditions of operation indicated its formation to be opposed by a reverse reaction, the speed of the latter increasing rapidly with rise of temperature. Warburg and Regener[6] had previously shown the silent discharge and the short wave-length radiations of sparks to possess both ozonizing and deozonizing properties and Regener[7] had shown that the deozonizing effect is produced by wave-lengths absorbed by glass but not by quartz. Regener found that a concentration of 2.2 per cent ozone could be produced by irradiating oxygen with the light from an aluminum spark, the chief intensity of which lies between 1719 and 1884A. The same stationary concentration was also produced when a gas containing a concentration of 6 per cent of ozone (prepared by the action of a silent discharge) was irradiated by the spark. The scant absorption data then available indicated that the ozone was chiefly formed by radiations of 2000A or less and that it was decomposed by wave-lengths between 2000 and 3000A.

Chapman, Chadwick and Ramsbottom[8] obtained considerable yields of ozone by the action of ultraviolet rays on partially dried oxygen, using a manometric method for following the reaction. At about this period several patents were granted for the production of ozone in various types of apparatus by the action of ultraviolet radiations.[9]

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[1] Schönbein, C., *J. prakt. Chem.*, **75**, 99 (1858).

[2] Nernst, W., *Jahresber. Elektr. Ges.*, 38 (**1894**), cited by Plotnikow, J., "Allgem. Photochemie," de Gruyter, Berlin, **1936**, 565.

[3] Lenard, P., *Ann. Physik*, **1**, 486 (1900).

[4] Goldstein, E., *Ber.*, **36**, 3042 (1903).

[5] Fischer, F., and Braehmer, F., *Ber.*, **38**, 2633 (1905).

[6] Warburg, E., and Regener, E., *Sitzber. K. Akad. Wiss. Berlin*, 1228, **1904**; *J. Chem. Soc.*, **86**, (ii), 692 (1904).

[7] Regener, E., *Ann. Physik*, **20**, 1033 (1906). For a recent theoretical discussion of the equilibrium between ozone formation and decomposition, see Eucken, A., and Patat, F., *Z. physik. Chem.*, **33B**, 459 (1936).

The formation of ozone in the vicinity of quartz mercury arcs is now a familiar observation. Dadlez[10] measured the diminution of the ozone content of the air at increasing distances from lamps of various makers to determine whether ozone is formed in sufficient amount to constitute a health hazard to operators of these lamps. He found that concentrations not greater than 0.05-0.3 mg. per cubic meter are produced under favorable conditions. Symptoms of distress are produced only when the concentration reaches 1.0 to 1.5 mg. per cubic meter and 4 mg. per cubic meter are necessary to render the atmosphere unsupportable to life. Nevertheless, Cornelius[11] recommended filtration to eliminate the rays forming ozone, at least in drying patent leather.

The formation of ozone by the shortest wave-lengths of the mercury arc, chiefly the 1850A line, may be now considered in the light of early work on the band spectra of oxygen. A series of bands in the Schumann region observed and measured by Schumann[12] and by Runge[13] are known as the Schumann-Runge bands. They begin at about 1925 to 2026A according to Leifson,[14] and converge to a limit at 1751A.[15] Detailed term analyses of these bands have been given by Ossenbrüggen.[16] Flory[17] believes the O_2 molecule predissociates in the band region above 1751A into normal ^3P atoms. Quantitative absorption data by Ladenburg, Van Voorhis and Boyce[18] and by Granath[19] indicate that the limit is followed by a region of continuous absorption which has its maximum at 1450A, and continues to nearly 1300A.[20] It has been subsequently shown that the products of the dissociation which occurs at or beyond 1751A are a normal ^3P and an excited ^1D oxygen atom.[21] Frerichs[22] found the excitation energy of the ^1D oxygen atom to be 1.96 e-volt. When this energy is deducted from that which corresponds to the convergence limit (7.05 volts), the heat of dissociation of oxygen into two normal atoms is found to be 5.09 e-volts, which corresponds to 117.3 kcal. or 2429A. Data on the kinetics of the reaction produced by the mercury line at 1850A are not available. Working with radiations of wave-lengths 1862 to 1719A, Eucken[23] found a negative temperature coefficient for the conversion of oxygen at very low pressures into ozone at temperatures between those of the room and liquid air.

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[8] Chapman, D. L., Chadwick, S., and Ramsbottom, J. E., *J. Chem. Soc.*, **91**, 947 (1907); see also Bordier, H., and Nogier, T., *Compt. rend.*, **147**, 354 (1908) and v. Aubel, E., *Ibid.*, **149**, 983 (1909); **150**, 96 (1910).

[9] Potter, H. N., U. S. P 854,965 May 28, 1907; Jaubert, G. F., French P. 415,574, July 19, 1909; Davis, N. W., U. S. P. 1,209,132, Dec. 19, 1916; *Chem. Abs.*, **11**, 549 (1917).

[10] Dadlez, J., *Compt. rend.*, **185**, 89 (1927); *L'Union Pharm.*, **69**, 17 (1928); *Chem. Abs.*, **23**, 2660 (1929).

[11] Cornelius, F., *Chim. et Ind.*, **6**, 218 (1921); German P. 318,065, Nov. 15, 1916.

[12] Schumann, V., *Smithsonian Contributions to Knowledge*, **29**, No. 1413 (1903).

[13] Runge, C., *Physica*, **1**, 254 (1921).

[14] Leifson, S. W., *Astrophys. J.*, **63**, 73 (1926); Hopfield, J. J., and Leifson, S. W., *Phys. Rev.*, **25**, 716 (1925).

[15] Birge, R. T., and Sponer, H., *Phys. Rev.*, **28**, 259, 270 (1926).

[16] Ossenbrüggen, W., *Z. Physik*, **49**, 167 (1928).

[17] Flory, P. J., *J. Chem. Physics*, **4**, 23 (1936).

[18] Ladenburg, R., Van Voorhis, C. C., and Boyce, J. C., *Phys. Rev.*, **40**, 1018 (1932); Ladenburg has also reviewed the work on absorption by atmospheric oxygen. *J. Opt. Soc. Am.*, **25**, 259 (1935).

[19] Granath, L. P., *Phys. Rev.*, **34**, 1046 (1929).

[20] Stueckelberg, E. C. G., *Phys. Rev.*, **42**, 518 (1932).

[21] Herzberg, G., *Z. physik. Chem.*, **4B**, 223 (1929).

[22] Frerichs, R., *Phys. Rev.*, **36**, 398 (1930).

[23] Eucken, A., *Z. physik. Chem.*, **107**, 436 (1923).

The absorption data thus far considered are not adequate to explain the results of Warburg on the formation of ozone by the irradiation of oxygen in a streaming system with the lines 2070 and 2530A.[24] These wave-lengths are longer than the Schumann-Runge bands and in order to secure sufficient absorption for a reaction to occur, it was necessary to employ the oxygen at high pressures. With the wave-length 2070A, Warburg found a quantum yield of 3.1 when the oxygen pressure was 125 kg. per square cm., and somewhat lower values at pressures as high as 300 kg. With the longer wave-length, 2530A, the quantum yields were somewhat lower and the same drop was observed with increase in pressure. Warburg attributed the decrease in yield with increase in pressure to some influence of adjacent molecules upon each other which affected their ability to absorb radiations. The absorption of the 2070A line was found to increase nearly seven times when the pressure was raised from about 30 to 325 kg. per square cm.[25] Noyes,[26] who has given a critical historical discussion of the reaction, believes, however, that the observed pressure effect on the quantum yield was not much greater than the possible experimental errors.

To account for the quantum yield of three, Warburg suggested, in the case of the 2070A line, a primary dissociation into atoms. This, however, is in disagreement with the subsequent findings upon the convergence limit of the Schumann-Runge bands. Warburg recognized that the 2530A line could not produce a dissociation of oxygen and suggested that a mechanism involving excited molecules would be necessary.

Further interpretations of the results of Warburg have been given by Wulf,[27] who has pointed out that the oxygen molecule does not absorb in the regions Warburg found effective. Certain weak bands which have been found in long paths of oxygen at ordinary pressures[28] and in compressed or liquid oxygen[29] appear to converge to a limit at 2429A. This agrees with the energy required for the dissociation of oxygen into normal atoms. The weak bands are followed by a weak continuous region which extends to shorter wave-lengths and even underlies the Schumann-Runge bands. Wulf believes that the light of wave-length 2070A, in Warburg's experiments was absorbed by this continuum. He ascribes the new bands, at least in part, to a van der Waals molecule, O_4, the presence of which in highly compressed oxygen had previously been suggested by Lewis[30] from a consideration of the magnetic susceptibility of oxygen at low temperatures. In support of this, Wulf cites the fact that the absorption intensity at 2470A increases as the square of the oxygen pressure. From an extrapolation of data of Liveing and Dewar,[31] he computed the region of the beginning of the continuous spectrum following the bands to be near 2470A, which he thought might correspond to dissociation into an ozone molecule and an oxygen atom. Guillien[32] also interprets data on the absorption of liquid oxygen as indicative of an equilibrium between O_2 and O_4 molecules. A set of bands lying in the region of the convergence of the Herzberg bands has been found by Finkelnburg and Steiner[33] to vary in intensity with the square of the pressure, although they attributed the effect to the proximity of two oxygen molecules rather than to the formation of O_4.[34] The arguments for and against polymerization have been critically discussed by Wulf.[35] A final conclusion between the possibility of the existence of O_4 and absorption by a pair of O_2 molecules during collision has not been reached. Steiner[36] does not believe the oxygen molecule should be considered a free radical, despite its paramagnetism, since the spin interaction between two oxygen molecules has a very low energy, not of the order of magnitude involved in chemical reaction.

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[24] Warburg, E., *Sitzb. Akad. Wiss.*. 216 (**1912**); 872 (**1914**); *Z. Elektrochem*, **27**, 133 (1921).

[25] Warburg, E., *Sitzb. Akad. Wiss. Berlin*, 230, **1915**; *J. Chem. Soc.*, **118** (ii), 404 (1920).

[26] Noyes, W. A., Jr., *Rev. Modern Physics*, **5**, 283 (1933).

[27] Wulf, O. R., *Proc. Nat. Acad. Sci.*, **4**, 356 (1928); **14**, 609 (1928); *J. Opt. Soc. Am.*, **25**, 231 (1935).

[28] Herzberg, G., *Naturwiss.*, **20**, 577 (1932).

[29] Ciechomski, L., *Beibl. Ann. Physik*, **39**, 240 (1915); Shaver, W. W., *Proc. Roy. Soc. Canada*, **15**, (III), 7 (1921). For the absorption of solid oxygen, see Prikhot'ko, A., Ruhemann, M., and Federitkenko, A., *Physik. Z. Sowjetunion*, **7**, 410 (1935); *Chem. Abs.*, **29**, 6141 (1935).

[30] Lewis, G. N., *J. Am. Chem. Soc.*, **46**, 2027 (1924).

[31] Liveing, G. D., and Dewar, Sir J., *Proc. Roy. Soc.*, **46**, 222 (1889).

[32] Guillien, R., *Compt. rend.*, **198**. 1486 (1934).

It has been claimed by Dickinson and Sherill[37] that the formation of ozone at atmospheric pressure can be stimulated by the presence of excited mercury atoms. Collision of an oxygen molecule with an excited mercury atom can give it nearly the energy necessary for dissociation into normal atoms[37a] or the excited mercury atom may on collision produce an excited oxygen molecule.

Radiations passing through fluorite (average wave-length 1750A and therefore close to or shorter than the convergence limit of the Schumann-Runge bands) form ozone in oxygen at atmospheric pressure with a quantum efficiency of two.[38] In the region of the bands the primary process has been believed to be the formation of an excited molecule followed by reactions as indicated in the scheme:

$$O_2 + h\nu \longrightarrow O_2^*$$
$$O_2^* + O_2 \longrightarrow O_3 + O$$
$$O + O_2 \longrightarrow O_3$$

The latter two processes are assumed to occur on the walls or as a result of triple collisions. In the region of continuous absorption, two oxygen atoms, one excited (^1D) are produced, and each then is assumed to combine with an oxygen molecule. If, as Flory suggests, the primary process is one of predissociation, the first equation would yield oxygen atoms directly, eliminating the necessity for the second equation.

The Decomposition of Ozone. Ozone possesses absorption bands both in the visible and in the ultraviolet regions and decomposition can be effected by absorption of light in either of these regions. Although the first investigations were conducted in the ultraviolet range, it is simplest to begin with the effects of visible light.

Ladenburg and Lehmann[39] showed ozone to possess a group of visible absorption bands,[40] for which Colange[41] has given quantitative absorption data. The diffuseness of the bands indicates the occurrence of predissociation.

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[33] Finkelnburg, W., and Steiner, W., *Z. Physik,* **79,** 69 (1932).

[34] See also Steiner, W., *Trans. Faraday Soc.,* **30,** 34 (1934) and Salow, H., and Steiner, W., *Z. Physik,* **99,** 137 (1936).

[35] Wulf, O. R., *J. Am. Chem. Soc.,* **50,** 2596 (1928).

[36] Salow, H., and Steiner, W., *Nature,* **134,** 463 (1934).

[37] Dickinson, R. G., and Sherill, M. S., *Proc. Nat. Acad. Sci.,* **12,** 175 (1926); for a detailed discussion see Franck, J., *J. Phys. Chem. U.S.S.R.,* **5,** 1013 (1934).

[37a] Presumably the deficit is made up thermally.

[38] Vaughan, W. E., and Noyes, W. A., Jr., *J. Am. Chem. Soc.,* **52,** 559 (1930); Groth, W. [*Z. physik. Chem.,* **37B,** 307 (1937)] finds it 1.90 for the xenon lines 1295 and 1470A.

[39] Ladenburg, R., and Lehmann, E., *Ann. Physik,* **21,** 305 (1906).

[40] See also Wulf, O. R., *Proc. Nat. Acad. Sci.,* **16,** 508 (1930).

[41] Colange, G., *J. Phys. Radium,* **8,** 254 (1927).

[42] Griffith R. O., and Shutt, W. J., *J. Chem. Soc.,* **119,** 1948 (1921); **123,** 2752 (1923).

By the use of filters, Griffith and Shutt[42] concluded the most effective spectral regions to lie between 7600 and 6700A and between 6150 and 5100A. The decomposition rate was proportional to the square of the ozone concentration. They believed the reaction to be catalyzed by hydrogen. Some water formation was also observed in accordance with the reaction $H_2 + O_3 \rightarrow H_2O + O_2$. This latter reaction became predominant when the original ozone concentration was below 2.4 per cent. In the presence of carbon monoxide,[43] some carbon dioxide was produced in an analogous reaction, which, however, occurred to but a slight extent. The simple ozone decomposition was said to be catalyzed by foreign gases in the following decreasing order of effectiveness: hydrogen, (far more effective than the others), helium, argon, nitrogen, carbon monoxide, and carbon dioxide. These authors believed the mechanism of the decomposition to involve the formation of activated molecules of ozone. These were then thought to combine each with an ozone molecule in its ground state to form a complex which, on collision with other molecules, might dissociate to yield from each complex three oxygen molecules. The temperature coefficient of the reaction was found to increase with the wave-length.

Similar results were reported by Kistiakowsky,[44] who employed monochromatic light of 6200A, used mixtures containing up to 70 per cent of ozone and varied the total gas pressures from atmospheric down to 9 mm. He found the quantum yields to be greater than two, and a direct function of the amount of red light absorbed and of the effective pressure of ozone in the system. He believed that in the absence of other added gases oxygen acted as an effective deactivator of excited ozone molecules and that those gases which, like hydrogen, seemed to catalyze the decomposition, appeared to do so only because they were less effective inhibitors than oxygen.

Schumacher[45] proposed a mechanism involving a photodissociation of the ozone into an oxygen molecule and an oxygen atom. Visible light is energetically capable of effecting this process, which requires 24.6 kcal., although this was not known at the time of Kistiakowsky's first paper. The foreign gas inhibitions were attributed to their specific effects on the recombination of the dissociation products to form ozone in three-body collisions. In the case of hydrogen, an interaction of the oxygen atom with the hydrogen molecules to form water was suggested as the cause of the ten-fold increase in the velocity of the ozone decomposition.

The strong absorption of ozone in the ultraviolet region has been the subject of numerous investigations, some of which have been discussed in Chapter 10. The maximum lies at about 2550A. According to Wulf and Melvin,[46] the spectrum appears partly banded and partly continuous; the bands, of which there are 23 of weak intensity between 3050 and 3400A, become sharper at low temperatures. Schumacher[47] believes an underlying continuum may be due to dissociation into an oxygen molecule in the ground state and an excited oxygen atom, or *vice versa*. Kondratjew[48] suggests that at wave-lengths less than 2700A both dissociation products may be in excited states. Mecke,[49] admits this possibility but places the wave-length limit at 2655A.[50]

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[42] Griffith, R. O., and McWillie, J., *J. Chem. Soc.*, **123**, 2767 (1923); Griffith, R. O., and McKeown, A., *Trans. Faraday Soc.*, **21**, 597 (1926).

[44] Kistiakowsky, G. B., *Z. physik. Chem.*, **117**, 337 (1925)

[45] Schumacher, H. J., *J. Am. Chem. Soc.*, **52**, 2377 (1930); Schumacher, H. J., and Sprenger, G., *Z. physik. Chem.*, **11B**, 38 (1930); *Z. Elektrochem.*, **38**, 620 (1932).

[46] Wulf, O. R., and Melvin, E. H., *Phys. Rev.*, **38**, 333 (1930).

[47] Schumacher, H. J., *J. Am. Chem. Soc.*, **52**, 2389 (1930).

[48] Kondratjew, V., *Z. physik. Chem.*, **7B**, 70 (1930); Jakolewa, A., and Kondratjew, V., *Physik. Z. Sowjetunion*, **1**, 472 (1932).

Early observations upon the rate of the decomposition of ozone in ultraviolet light were reported by v. Bahr[51] and by Weigert.[52] In the presence of hydrogen, a catalysis was observed.

Using the wave-length 2530A, Warburg[53] measured the quantum yield of the reaction under various conditions. For low concentrations of ozone, about 0.5 per cent or less, the yield was 0.28. It was considerably greater in the presence of nitrogen (1.1) or helium (1.7). For high ozone concentrations, the yields increased to 3.5 at 9 per cent. With moist ozone at about this concentration, the use of the wave-length 2090A gave a quantum yield as high as 8, suggesting a chain reaction.

Schumacher and Beretta[54] find the mechanism of the reaction due to the wave length 3130A to be similar to that occurring in red light. Heidt and Forbes[55] find from the magnitude of the quantum efficiency of the decomposition of pure, dry ozone that even in the absence of water vapor the reaction produced by 2080, 2540 or 2800A has chain characteristics. The yields were frequently above two, sometimes four and even as high as 6.7. The quantum efficiency increased with the partial pressure of ozone and decreased with that of oxygen. No dependence of the quantum yield upon the wave-length was observed. The temperature coefficient was 1.2, or possibly slightly greater at very low temperatures. Heidt[56] later found approximately the same quantum yields at 3130A as at 2080A.

The Chlorine-Sensitized Decomposition of Ozone. In regions in which ozone does not absorb, its decomposition can be brought about by the addition of chlorine as a photosensitizer. This reaction was discovered by Weigert,[57] who concluded its rate to be proportional to the light absorbed by the chlorine and independent of the ozone concentration. Bonhoeffer[58] found the absorption of one quantum (4360 or 4050A) to produce the decomposition of two molecules of ozone. More recent observations by Allmand and Spinks[59] have shown quantum yields as high as 30 (in some cases 59) at high ozone concentrations. Under these conditions the rate of reaction is proportional to the square root of the light intensity. Schumacher and Wagner[60] suggested the formation of ClO as an intermediate product in this reaction, and Bodenstein, Harteck and Padelt[61] gave evidence for the formation of some ClO_3. There are many complicating features, as an induction period (not observed by Weigert) and after effects. Allmand and Spinks suggested that chlorine atoms, formed in the primary absorption process, may combine to ClO_3 on collision with ozone molecules and that a chain reaction may ensue and be terminated by the absorption of intermediate atoms or groups on the walls. Furthermore, some ClO_3 molecules may unite to form chlorine hexoxide which in the presence of water forms chloric and perchloric acids. The combination of Cl atoms and oxygen molecules may also give rise to ClO_2. The latter, reacting with ozone, forms oxygen molecules and ClO_3 groups.

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[49] Mecke, R., *Z. physik. Chem. Bodenstein Festband*, 392 (1931).

[50] For further details on the absorption spectrum of ozone in the ultraviolet, see Lauchli, A., *Helv. phys. Acta,* **1,** 232 (1928); *Z. Physik,* **53,** 92 (1929); Dutheil, J. and M., *J. Phys. Radium,* **7,** 415 (1926); Cabannes, J., and Dufay, J., *J. Phys. Radium,* **7,** 257 (1926); Chalonge, D., and Lambrey, M., *Compt. rend.,* **184,** 1165 (1927); Tsi-Zé, N., and Shin-Piaw, C., *Compt. rend.,* **195,** 309 (1932); Vassy, E., *Compt. rend.,* **202,** 1426 (1936).

[51] v. Bahr, E., *Ann. Physik,* **33,** 598 (1910).

[52] Weigert, F., *Z. physik. Chem.,* **80,** 78 (1912); *Ber.,* **46,** 815 (1913); Weigert, F., and Böhm, H., *Z. physik. Chem.,* **90,** 189 (1915).

[53] Warburg, E., *Sitzb. Preuss. Akad.,* 644 (1913).

[54] Schumacher, H. J., and Beretta, U., *Z. physik. Chem.,* **17B,** 405, 417 (1932); Ritchie, M., *Proc. Roy. Soc.,* **146A,** 848 (1934).

[55] Heidt, L. J., and Forbes, G. S., *J. Am. Chem. Soc.,* **56,** 2365 (1934).

[56] Heidt, L. J., *J. Am. Chem. Soc.,* **57,** 1710 (1935).

[57] Weigert, F., *Ann. Physik,* **24,** 243 (1907); *Z. Elektrochem.,* **14,** 591 (1908).

[58] Bonhoeffer, K. F., *Z. Physik,* **13,** 94 (1923).

[59] Allmand, A. J., and Spinks, J. W. T., *Nature,* **124,** 651 (1929); *J. Chem. Soc.,* 1652 (**1931**); 599 (**1932**).

[60] Schumacher, H. J., and Wagner, C., *Z. physik. Chem.,* **5B,** 199 (1929).

[61] Bodenstein, M., Harteck, P., and Padelt, E., *Z. anorg. Chem.,* **147,** 233 (1925).

Heidt, Kistiakowsky and Forbes[62] found highly abnormal temperature coefficients ranging from 0.7 to 14.6. The purer the gases the more erratic were the results and the more prominent a "fast" reaction in the dark following a brief exposure to light. A marked decrease in the rate with the time of illumination was also observed. No mechanism could be proposed capable of explaining the results. In a subsequent investigation, Norrish and Neville[63] observed a red liquid oxide of chlorine $(ClO_3)_n$ and suggested that its separation and slow decomposition might in some manner account for the observations of Heidt, Kistiakowsky and Forbes. Norrish and Neville found that at low ozone concentrations, the reaction is of zero order and has a chain mechanism. At high ozone concentrations, in agreement with Allmand and Spinks, the rate was proportional to the square root of the light intensity (3650A). At high concentrations of oxygen and chlorine, the rate was proportional to the first power of the intensity and the reaction was inhibited. The quantum yields varied from two to about ten. Chains may be propagated both by chlorine atoms and by ClO radicals. Nitrogen and carbon dioxide appeared to have no effect on the reaction. Rollefson and Byrns[64] isolated ClO_3 from the reaction mixture and noted that its occurrence therein prevents pressure measurements from affording an accurate indication of the amount of ozone decomposed. They also produced evidence for a reaction mechanism involving Cl_2O_7.

The chlorine-sensitized decomposition of ozone was used in actinometry by Cremer[65] since when low ozone concentrations are employed and light absorbed only by chlorine is used, the quantum yield is generally found to be two. Even in carbon tetrachloride solution, quantum yields of two have been observed for both the unsensitized and the sensitized ozone decompositions.[66]

The effect of irradiation of ozone-chlorine mixtures by wave-lengths absorbed by the ozone rather than by the chlorine has been investigated by Bodenstein and Schumacher,[67] who proposed a mechanism involving directly excited ozone molecules. These were thought to react with chlorine molecules with the formation of the ClO radical and ClO_2. They found also that chlorine hexoxide was produced and that its yield could be increased by lowering the temperature or by increasing the size of the reaction vessel.

THE FORMATION AND DECOMPOSITION OF WATER

Absorption. Water vapor commences to absorb light quite suddenly at about 1800A.[68] Rathenau[69] found predissociation bands between 1780 and 1540A and again at 1340A. Mecke[70] believes there is a series of bands converging at 1390A, corresponding to a dissociation into an excited hydroxyl radical and a hydrogen atom. A continuous region near 1800A may correspond to a dissociation into a hydrogen atom and a normal state hydroxyl radical. Quantitative data on the absorption of water in the longer wave-length ultraviolet and in the visible have been given by Granath[71] and by Dawson and Hulburt.[72]

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[62] Heidt, L. J., Kistiakowsky, G. B., and Forbes, G. S., *J. Am Chem. Soc.*, **55**, 223 (1933).

[63] Norrish, R. G. W., and Neville, G. H. J., *Nature*, **131**, 544 (1933); *J. Chem. Soc.*, 1864 (1934).

[64] Rollefson, G. K., and Byrns, A. C., *J. Am. Chem. Soc.*, **56**, 364 (1934).

[65] Cremer, E., *Z. physik. Chem.*, **128**, 285 (1927).

[66] Bowen, E. J., Moelwyn-Hughes, E. A., and Hinshelwood, C. N., *Proc. Roy. Soc*, **134A**, 211 (1931).

[67] Bodenstein, M., and Schumacher, H. J., *Z. physik. Chem.*, **5B**, 233 (1929).

[68] [1830A in 17 mm. layers of liquid water, Kreusler, H., *Ann. Physik*, **6**, 412 (1901)]; Leifson, S. W., *Astrophys. J.*, **63**, 73 (1926); Goodeve, C. F., and Stein, N. O., *Trans. Faraday Soc.*, **27**, 193 (1931).

[69] Rathenau, G., *Z. Physik*, **87**, 32 (1933).

According to Plotnikow, the first observation of the photo-chemical decomposition of water into hydrogen and oxygen was made by Baker.[73] Similar observations were made by early workers with the quartz mercury arc.[74] Tian,[75] who obtained traces of hydrogen peroxide, clearly recognized that only the shortest waves passing through quartz were capable of effecting the decomposition of water. Dhar[76] believes water vapor in the upper atmosphere to be decomposed by the solar ultraviolet.

Coehn[77] described the production of a stationary state in which irradiation of water vapor caused a decomposition of 0.2 per cent; the decomposition increased with the light intensity and decreasing pressure. Andrejeff,[78] however, found that at 200°C., in the stationary state, decomposition had proceeded to only 0.002 per cent. No theoretical studies from the modern viewpoint are available.

The formation of hydrogen peroxide from water and oxygen by ultraviolet rays has been observed. It appeared to depend largely upon special experimental conditions or possibly upon the presence of impurities.[79]

Earlier workers claimed to have been able to induce the combination of hydrogen and oxygen by exposure to the ultraviolet radiations of a mercury arc. Although Thiele[80] believed the presence of moisture not to be necessary for the combination to occur, Baker and Carlton[81] were unable to observe any contraction during irradiation for five or six hours of gases which had been dried several weeks. Wet gases showed a certain amount of reaction during the same period of irradiation.

Kistiakowsky[82] investigated the reaction in two wave-length regions, the source being a condensed spark between aluminum disk electrodes. When the lines about 1720A, that is, within the continuous absorption region of oxygen, were employed, the yield of ozone in the presence of hydrogen was only one-fourth of that in the presence of nitrogen and an equal amount of hydrogen peroxide was also formed. The ozone yields were proportional to the relative concentrations of oxygen in the hydrogen-oxygen mixture, and the yields of hydrogen peroxide were proportional to the concentration of hydrogen. In the more recent experiments it was found that in the presence of increasing concentrations of hydrogen, the ozone yield decreased to zero and the yield of hydrogen peroxide increased. At high pressures, the yield of water parallels that of hydrogen peroxide. At lower pressures, the yield of water also increases, although not at the expense of ozone or peroxide. In a one to one oxygen-hydrogen mixture, the rates at which the excited oxygen atoms react with oxygen or hydrogen are nearly equal. The following system of partial reactions was suggested:

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[70] Mecke, R., *Trans. Faraday Soc.*, **27**, 369 (1931).

[71] Granath, L. P., *Phys. Rev.*, **34**, 1046 (1929).

[72] Dawson, L. H., and Hulburt, E. O., *J. Opt Soc. Am.*, **24**, 175 (1934).

[73] Baker, H. B., *Proc. Chem. Soc.*, **18**, 40 (1902).

[74] Fischer, F., and Braehmer, F., *Ber.*, **79**, 958 (1906); Thiele, H., *Ber.*, **40**, 4914 (1907); *Z. angew. Chem.*, **22**, 2472 (1909); Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1191 (1910); **152**, 522 (1911); Smits, A., and Aten, A., *Z. Elektrochem.*, **16**, 264 (1910).

[75] Tian, A., *Compt. rend.*, **152**, 1483 (1911); **151**, 1040 (1911).

[76] Dhar, N. R., *Trans. Faraday Soc.*, **30**, 142 (1934).

[77] Coehn, A., *Ber.*, **43**, 880 (1910).

[78] Andrejeff, I., *Z. Elektrochem.*, **19**, 551 (1913).

[79] Kernbaum, M., *Compt. rend.*, **148**, 705 (1909); **149**, 116, 273 (1909).

[80] Thiele, H., *Z. angew. Chem.*, **22**, 2472 (1909).

[81] Baker, H. B., and Carlton, M., *J. Soc. Chem. Ind.*, **44**, 1047 (1925).

[82] Kistiakowsky, G B., *J. Am. Chem. Soc.*, **52**, 1868 (1930); Kistiakowsky, G. B., and Smith, H. A., *Ibid.*, **57**, 835 (1935).

$$\begin{aligned} O + O_2 &\longrightarrow O_3 && (1)\\ O + H_2 &\longrightarrow OH + H && (2)\\ H + O_2 &\longrightarrow HO_2 && (3)\\ OH + OH &\longrightarrow H_2O_2 && (4)\\ HO_2 + HO_2 &\longrightarrow H_2O_2 + O_2 && (5)\\ OH + HO_2 &\longrightarrow H_2O + O_2 && (6) \end{aligned}$$

It was believed that (2) did not occur readily, the hydrogen molecule showing an unexpected stability. However, the possibility that oxygen atoms might unite with hydrogen in three-body collisions with oxygen molecules appeared to be admissible, (2) and (3) occurring together as

$$O + O_2 + H_2 \longrightarrow OH + HO_2.$$

Kistiakowsky and Smith believed, contrary to Ritchie,[83] that reaction (1) has an activation energy of zero. Nevertheless, the formation of ozone was also thought to take place in triple collisions

$$O + O_2 + O_2 \longrightarrow O_3 + O_2.$$

In later experiments (1935) it was possible to demonstrate the formation of hydrogen peroxide which had been missed in the earlier experiments (1930), even when wave-lengths of the band region (1854-1862A) were alone employed, the strong aluminum lines at 1720A being removed by an oxygen filter. The yield, however, was only half that produced in the experiments with shorter wave-lengths. It appeared that one-half of the absorbed light of the longer wave-lengths forms ozone irrespective of the composition of the gases, the other half giving rise to the same sequence of reactions as occur under shorter wave-length illumination. To explain this, the primary process was assumed to be the formation of excited oxygen molecules which react with oxygen molecules[84] to give ozone and atomic oxygen, but which suffer only elastic collisions with hydrogen. No attempt was made to determine the rate of water formation in this region.

Flory[85] suggests that in the band region predissociation of oxygen produces two normal state oxygen atoms, and that the differences in the reaction as conducted in the band and continuous regions are to be attributed to the different states of the oxygen atoms formed by predissociation and by dissociation.

Neuĭmin and Popov[86] also studied the reaction in the Schumann region, using hydrogen at 0.1 mm. pressure, and found quantum yields (for peroxide formation) of approximately 0.1. Their mechanism was similar to that subsequently given by Kistiakowsky, except that they believed that in the reaction between excited oxygen atoms and hydrogen molecules, the hydroxyl radical formed (along with a hydrogen atom) was excited with vibrational energy up to 2 electron-volts. They also assumed that the combination of two hydroxyl radicals was a wall reaction. Miyanishi[87] studied the influence of temperature upon the reaction. Kistiakowsky found the formation of water to be greatly increased at high temperatures.

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[83] Ritchie, M., *Proc. Roy. Soc.*, **146A**, 848 (1934).

[84] See also Klemenc, A., and Patat, F., *Naturwiss.*, **18**, 281 (1930).

[85] Flory, P. J., *J. Chem. Physics*, **4**, 23 (1936).

[86] Neuĭmin, H., and Popov, B., *Z. physik. Chem.*, **27B**, 15 (1934). For more recent studies with the xenon lamp, see W. Groth and P. Harteck, *Z. Elektrochem.*, **44**, 621 (1938).

The Mercury-Sensitized Reaction. (See also page 257, chapter 16.) Marshall[88] investigated the mercury-sensitized reaction of hydrogen and oxygen. At 50°C., the fall in pressure of dried gas mixtures ranging in composition from 406 mm. hydrogen and 148 mm. oxygen to 572 mm. hydrogen and 156 mm. oxygen, was 24.7 mm. per minute. The pressure-time curves showed an initial break at a point corresponding with saturation of the gas with water-vapor, after which the curves were linear. When oxygen was present in excess, the rate decreased rapidly as the reaction proceeded. However, in the reaction of stoichiometric mixtures, the rate remained constant. Marshall believed the true temperature coefficient to be near unity, but experimentally many corrections were necessary because the concentration of mercury vapor varied with the temperature and because the quantum yield varied with temperature. For the formation of hydrogen peroxide, the quantum yield was found to be 2.5.[88a] At least 75 per cent of the total yield of products was peroxide. The mechanism suggested involved the reactions,

$$Hg^* + H_2 \longrightarrow Hg + 2H \qquad (1)$$

$$H + O_2 \longrightarrow HO_2 \qquad (2)$$

$$HO_2 + H_2 \longrightarrow H_2O_2 + H \qquad (3)$$

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \qquad (4)$$

Marshall[89] later found the optimum mercury vapor pressure for the formation of hydrogen peroxide to be 0.005 mm. The greater rate of reaction in the presence of higher concentrations of mercury was offset by decomposition of the hydrogen peroxide formed. The rate of the reaction probably varied as the first power of the light intensity. The maximum rate of formation of hydrogen peroxide was 2 gm. per hour.

Frankenburger and Klinkhardt,[90] obtained somewhat different quantum yields at room temperature. The quantum yield for water was greater (1.5-2.5) and that for hydrogen peroxide lower (1-2). They objected to the mechanism proposed by Marshall for the formation of hydrogen peroxide (Reactions 2 and 3) on the ground that the reaction $HO_2 + H_2 \longrightarrow H_2O_2 + H$ is endothermic by 31 kcal. Barak and Taylor reported that this conclusion was based upon an unwarranted assumption, and stated that reactions 2 and 3 are together exothermic. Farkas and Sachsse[91] have shown that hydrogen atoms react with O_2 molecules to produce HO_2 by three-body collisions. It is necessary to build up a mechanism of the type devised by Marshall if the quantum yield of hydrogen peroxide is really two or greater, since a chain mechanism is demanded. If, however, as Frankenburger found, the yield is lower, a chain mechanism is not necessary. Then, however, it would be necessary to account for the higher yields of water, assumed to be formed directly and not through hydrogen peroxide, by a chain mechanism, as one proposed by Bonhoeffer and Haber.[92] Frankenburger and Klinkhardt assumed the hydrogen peroxide to be formed by the union of two OH radicals in a three-body collision. Bates,[93] suggested that the discrepancy between the results of Frankenburger and Klinkhardt and those of Marshall may be due to the fact that the former workers used a light intensity a hundred-fold greater than that employed by Marshall. Bates favored the Marshall mechanism.

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[87] Miyanishi, M., *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **26**, 70 (1935); *Chem. Abs.*, **29**, 2852 (1935).

[88] Marshall, A. L., *J. Phys. Chem.*, **30**, 34, 1078 (1926); Taylor, H. S., and Marshall, A. L., *Ibid.*, **29**, 842, 1140 (1925).

[88a] This represented a correction of an earlier value of 6.6, in error because of the use of an incorrect value for the transmission of the filter.

[89] Marshall, A. L., *J. Am. Chem. Soc.*, **49**, 2763 (1927).

[90] Frankenburger, W., and Klinkhardt, H., *Trans. Faraday Soc.*, **27**, 431 (1931); *Z. physik. Chem.*, **15B**, 421 (1932); see also Barak, M., and Taylor, H. S., *Trans. Faraday Soc.*, **28**, 569 (1932).

[91] Farkas, L., and Sachsse, H., *Z. physik. Chem.*, **27B**, 111 (1934).

The amount of mercuric oxide formed in the course of the reaction may exert a considerable effect upon the rate and may influence the results. Noyes [94] found no appreciable reaction between mercury and normal state oxygen atoms. But under conditions in which ozone may be formed, there is a reaction. Noyes also suggested the possibility of the formation of a relatively unstable complex (between excited mercury atoms and oxygen)which may be converted into ozone on collision with oxygen molecules. Franck [95] finds that at pressures of oxygen below 1 cm., the formation of mercuric oxide initiated by excited mercury atoms is proportional to the incident intensity of the resonance line of mercury and to the number of damped collisions of mercury with oxygen. Also, the formation of the oxide was said to be independent of the presence of shorter wave-lengths in the incident radiation. At greater oxygen pressures, mercury oxide is formed when oxygen molecules alone are excited by the lines 1860, 1935 and 1990A, which produce ozone. Therefore, excited mercury is not necessary for the synthesis of mercuric oxide in the presence of ozone.[96]

The velocity of the photosensitized reaction between hydrogen and oxygen is slightly higher than that between deuterium and oxygen, but the temperature coefficients of the two reactions seem to be identical.[97]

The formation of water may also be sensitized by substances other than mercury. The formation of water during the combination of hydrogen and chlorine may be regarded as a reaction in which chlorine is the photosensitizer. In this reaction, Cremer [98] found the rate of formation of water to be proportional to the chlorine concentration. He suggested that an excited chlorine atom could pass its excitation energy over to an oxygen molecule, as could an excited Cl_2 molecule. The excited oxygen molecules might then react to form water by the process: $O_2^* + 2H_2 \longrightarrow 2H_2O$. Norrish [99] doubted this mechanism, since he believed the low excitation energy of the metastable chlorine atom would be insufficient to activate the oxygen molecule sufficiently to enable the latter to react with hydrogen. He stated that the inhibiting effect of oxygen on the hydrogen-chlorine combination is due to the reaction of molecules of oxygen with hydrogen atoms of the chain to form OH radicals. The latter can combine at ordinary temperatures to hydrogen peroxide. He found the peroxide to be produced in appreciable quantities when mixtures of oxygen, hydrogen and chlorine at atmospheric pressure were irradiated with light from a mercury arc. Also, it was stated[100] that if the partial pressure of chlorine in the mixture is above a certain critical value (temperatures between 0° and 300°C.) exposure of the mixture in glass to the light from a mercury vapor lamp will result in a practically instantaneous explosion with quantitative conversion of the hydrogen and oxygen to water. Below this partial pressure of chlorine, a rapid reaction between the hydrogen and chlorine occurs, only a trace of water being formed. The limiting pressure of chlorine increases rapidly as the lower temperatures are approached. His mechanism involved the reactions:

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[92] Bonhoeffer, K. F., and Haber, F., *Z. physik. Chem.*, **137A**, 263 (1928).

[93] Bates, J. R., *J. Am. Chem. Soc.*, **55**, 426 (1933); *J. Chem. Physics*, **1**, 457 (1933).

[94] Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **49**, 3104 (1927); *Z. physik. Chem.*, **2B**, 445 (1929).

[95] Franck, J., *Compt. rend. Acad. Sci. U.R.S.S.*, **4**, 146 (1933); *Brit. Chem. Abs.*, **A**, 263 (1934); *Acta Physicochim. U.R.S.S.*, **1**, 833 (1934); *J. Phys. Chem. (U.S.S.R.)*, **5**, 1013 (1934); *Chem. Abs.*, **29**, 6507 (1935).

[96] It is also possible for the excited mercury atoms to produce some dissociation of water molecules, when and if present, into hydrogen atoms and normal state hydroxyl radicals. Senftleben, H., and Rehren, I., *Z. Physik*, **37**, 529 (1926); Gaviola, E., *Temas de quim.*, **2**, 173 (1929); *Chem. Abs.*, **24**, 2376 (1930).

[97] Evans, M. G., *J. Chem. Physics*, **2**, 726 (1934).

[98] Cremer, E., *Z. physik. Chem.*, **128**, 285 (1927).

[99] Norrish, R. G. W., *Trans. Faraday Soc.*, **27**, 461 (1931).

$$H + H_2 + O_2 \longrightarrow OH + H_2O$$
$$OH + H_2 \longrightarrow H + H_2O.$$

It was reported that the second of these reactions cannot occur spontaneously at temperatures below 400°C. In answering certain objections of Semenoff,[101] Norrish stated that for an explosion to occur, a small volume element of the mixture must become heated to 600°C.

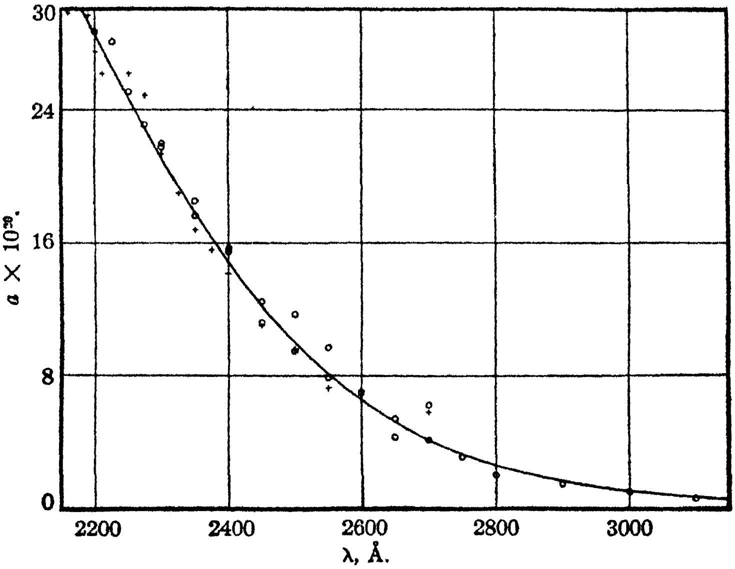

FIGURE 112. Absorption by Hydrogen Peroxide (Urey, Dawsey, and Rice, *Journal American Chemical Society*). + = vapor; o = solution.

Certain nitrogen compounds may also sensitize the reaction of hydrogen and oxygen. Farkas, Haber and Harteck[102] found small quantities of ammonia to increase the reaction velocity at temperatures between 120°C. and 420°C. with and without irradiation by a zinc spark.[103] Taylor and Salley[104] measured the temperature coefficients of the mercury-sensitized and of the ammonia-sensitized reactions at high temperatures. The results indicated that in the presence of ammonia long reaction chains occur above 300°C, but that in the mercury-sensitized reaction lengthening of the chains occurs only above 490°C. The chains may be propagated by atomic hydrogen, amino-radicals, or intermediate oxidation products.

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[100] Norrish, R. G. W., *Nature*, **127**, 853 (1931); *Proc. Roy. Soc.*, **135A**, 334 (1932); *Physik. Z. Sowj.*, **3**, 225 (1933).

[101] Semenoff, N., *Physik. Z. Sowj.*, **3**, 225 (1933).

[102] Farkas, L., Haber, F., and Harteck, P., *Naturwiss.*, **18**, 266 (1930).

[103] See also Taylor, H. S., and Bates, J. R., *Nature*, **125**, 599 (1930) for the formation of atomic hydrogen by the photodissociation of ammonia.

[104] Taylor, H. S., and Salley, D. J., *J. Am. Chem. Soc.*, **55**, 96 (1933).

Nitrogen peroxide functions also in photochemical combination of hydrogen and oxygen. On absorption of light the peroxide dissociates into NO and O which then start the reaction chain between hydrogen and oxygen.[105]

The Decomposition of Hydrogen Peroxide. Urey, Dawsey and Rice[106] determined the coefficients of absorption of hydrogen peroxide vapor at room temperature (Figure 112). The continuous nature of the curve indicates a dissociation of the molecules. The peroxide molecule was regarded as formed of two OH radicals. From thermochemical data it did not appear possible to choose between the following methods of dissociation: (a) into 2OH, (b) into H and HO_2 and (c) into H_2O and O. The first possibility was favored since the emission spectrum of hydrogen peroxide, streamed rapidly through a cool discharge tube, was predominantly that of OH. Since illumination of hydrogen peroxide vapor with the zinc spark lines (2025-2138A) caused the water bands (OH) to appear in fluorescence, it was concluded that the following reaction must occur:

$$H_2O_2 + h\nu \longrightarrow OH(^2P) + OH(^2S)$$

For wave-lengths between 2200 and 3000A, there was favored the reaction

$$H_2O_2 + h\nu \longrightarrow OH(^2P_{1/2}) + OH(^2P_{3/2}).$$

Sharma,[107] however, states that reduction of cupric oxide on irradiation in an absorption tube with hydrogen peroxide indicates the formation of atomic hydrogen (process b).

A mixture of 1 per cent hydrogen peroxide in carbon monoxide when circulated at 40° past a quartz window transmitting the wave-lengths 2070 and 2530A produced carbon dioxide by a slow reaction.[108]

When the carbon monoxide was replaced by hydrogen, water was formed. It was assumed that there was a primary decomposition of the peroxide into two hydroxyl radicals which then reacted slowly according to the mechanism proposed by Bonhoeffer and Haber[109] and by Lavin and Jackson.[110]

$$\begin{gathered} OH + H_2 \longrightarrow H_2O + H \\ OH + CO \longrightarrow CO_2 + H. \end{gathered}$$

Had the photodissociation of the peroxide yielded instead water and an oxygen atom (process c), no interaction with hydrogen or carbon monoxide should have been observed, since the oxygen atoms would be expected to react much faster with hydrogen peroxide than with hydrogen or carbon monoxide. The reaction between OH and H_2 was considered to require an activation energy of not less than 14 kcal. This would keep the rate sufficiently small at temperatures below about 400° to make the predominant reaction

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[105] Norrish, R. G. W., and Griffiths, J. G. A., *Proc. Roy. Soc.*, **139A**, 147 (1933); Miyanishi, M., *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **27**, 47 (1935); *Chem. Abs.*, **29**, 5351 (1935).

[106] Urey, H. C., Dawsey, L. H., and Rice, F. O., *J. Am. Chem. Soc.*, **51**, 1371 (1929). See also Fergusson, W. C., Slotin, L., and Style, D. W. G., *Trans. Faraday Soc.*, **32**, 956 (1936).

[107] Sharma, R. S., *Proc. Acad. Sci. United Provinces Agra Oudh, India*, **4**, 51 (1934); *Chem. Abs.*, **29**, 7187 (1935).

[108] v. Elbe, G., *J. Am. Chem. Soc.*, **54**, 822 (1932); **55**, 62 (1933).

[109] Bonhoeffer, K. F., and Haber, F., *Z. physik. Chem.*, **137A**, 263 (1928).

[110] Lavin, G. I., and Jackson, W. F., *J. Am. Chem. Soc.*, **53**, 383, 3189 (1931).

$$OH + OH + M \longrightarrow H_2O_2 + M.$$

But from consideration of the data obtained at various partial pressures and temperatures it was believed that this last reaction ought to be excluded. Accordingly, the results were regarded by v. Elbe as not sustaining the reaction scheme proposed for the mercury-sensitized hydrogen-oxygen reaction by Frankenburger and Klinkhardt which involved the recombination of 2OH to H_2O_2.[111]

The Photo-Oxidation of Hydrogen Iodide. Bates and Lavin[112] studied this reaction at pressures of 50-100 mm. of hydrogen iodide and 150-500 mm. of oxygen at 0°C. Their results led to the conclusion that the quasi-molecule HO_2 may have a life of 10^{-8} or 10^{-9} second, much longer than is usually assigned to such complexes. Kondrat'ev, Kondrat'eva and Lauris[113] studied the effects of irradiating various mixtures of hydrogen iodide and oxygen both in Uviol apparatus transmitting only wave-lengths longer than 2800A and in a quartz apparatus. A larger proportion of the hydrogen iodide was oxidized under the latter conditions. To explain the difference they assumed that in quartz along with the reaction $H + O_2 \longrightarrow HO_2$ there occurs the reaction $H + O_2 \longrightarrow OH + O$. Otherwise the results could be explained by assuming that the probability of occurrence of the reaction $H + O_2 \longrightarrow HO_2$ increases with an increase in the kinetic energies of the hydrogen atoms and oxygen molecules.

Bodenstein and Schenk[114] pointed out that the results of Bates and Lavin might be explained equally well on the assumption that the reaction between H and O_2 occurs as either two-body or three-body collisions. Kinetic studies by Cook and Bates[115] indicated the reaction to be of the latter type, the third body being chiefly either oxygen or hydrogen iodide molecules. The presence of an inert gas such as nitrogen speeds up the reaction. In similar experiments, it was shown that deuterium iodide is always more completely oxidized than is hydrogen iodide.

Winther[116] studied the rate of oxidation of hydriodic acid in the light and in the dark in various solvents.

PHOTOCHEMICAL REACTIONS OF THE OXIDES OF CHLORINE

Chlorine Monoxide. Balard, the discoverer of chlorine monoxide, observed its decomposition in light into chlorine and oxygen.[117] Bodenstein and Kistiakowsky[118] found that one absorbed quantum (4050 or 4360A) caused the decomposition of two molecules of the monoxide, whether the quantum was absorbed by chlorine monoxide or by some chlorine also present. The reaction was unaffected by the presence of air and the temperature coefficient was 1.09. Small amounts of chlorine dioxide were formed during the decomposition. Schumacher and Wagner[119] proposed a mechanism for the reaction in which ClO appears as an intermediate product.

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[111] Frankenburger, W., and Klinkhardt, H., *Trans. Faraday Soc*, **27**, 431 (1931); *Z. physik. Chem.* **15B**, 421 (1932).

[112] Bates, J. R., and Lavin, G. I., *J. Am. Chem. Soc.*, **55**, 81, (1933).

[113] Kondrat'ev, V., Kondrat'eva, E., and Lauris, A., *J. Phys. Chem. (U.S.S.R.)*, **5**, 1411 (1934); *Chem. Abs*, **29**, 7810 (1935).

[114] Bodenstein, M., and Schenk, P. W., *Z. physik. Chem*, **20B**, 420 (1933).

[115] Cook, G. A., and Bates, J. R., *J. Am. Chem. Soc.*, **57**, 1775 (1935); see also Kistiakowsky, G. B., and Smith, H. A., *Ibid.*, **57**, 835 (1935).

[116] Winther, C., *Z. physik. Chem.*, **113**, 275 (1924); **3B**, 299, 315 (1929); see also Plotnikow, I., *Ibid.*, **111**, 171 (1924).

[117] Balard, A., *Ann. Pharm.*, **14**, 167, 298 (1835).

[118] Bodenstein, M., and Kistiakowsky, G. B., *Z. physik. Chem.*, **116**, 371 (1925).

The absorption spectrum of chlorine monoxide is continuous from 2200 to 8500A, so that dissociation is implied. The extinction coefficients have different values in various wave-length regions. Attempts have been made to assign different dissociation processes to different wave-length regions.[120]

Goodeve and Wallace considered three types of dissociation, yielding respectively, Cl_2 and O, ClO and Cl, and Cl, Cl and O. Finkelnburg, Schumacher and Stieger, however, disregard the first possibility and believe that the absorption beginning at 6600A corresponds to the second of these possibilities of dissociation, the chlorine atom probably being excited. Maxima apparent at 5300 and at 4100A were attributed to the same dissociation products but in different states of excitation. Both groups of workers attribute the maximum at 2560A to dissociation into an oxygen atom and two chlorine atoms.

For the wave-lengths 436, 365 and 313 $m\mu$, the rate of decomposition is proportional to the amount of light absorbed, and therefore, independent of the chlorine pressure and also of the Cl_2O pressure until the latter falls below a certain limit. Finkelnburg, Schumacher and Stieger found a higher value than Bodenstein and Kistiakowsky for the quantum yield. It was about 3.5 and varied by only 10 per cent between the extreme wave-lengths. The temperature coefficient, (1.1 in agreement with Bodenstein and Kistiakowsky), increases as the temperature rises. The chain reaction observed was accounted for by the following processes:

$$Cl_2O + h\nu \longrightarrow ClO + Cl \qquad (1)$$
$$Cl + Cl_2O \longrightarrow Cl_2 + ClO \qquad (2)$$
$$ClO + Cl_2O \longrightarrow Cl_2 + O_2 + Cl \qquad (3)$$

Other intermediate products were noted to be ClO_2 and a brown higher oxide of chlorine of unknown composition. A smaller quantum yield observed when the reaction is conducted in solution in carbon tetrachloride[121] was explained by Finkelnburg, Schumacher and Stieger on the assumption that the recombination reactions

$$Cl + Cl \longrightarrow Cl_2$$
$$Cl + ClO \longrightarrow Cl_2O$$

occur so much more frequently in the solution than in the gaseous state that they compete effectively with reaction (2).

The use of shorter wave-lengths (2350-2750A) increases the quantum yield to 4.5 at 20°C.[122] The addition of hydrogen accelerates the decomposition, at least up to the stage at which the secondary reaction, $H_2 + Cl_2 \rightarrow 2HCl$, becomes prominent.[123] Chlorine and oxygen are the main products. Hydrogen atoms are not as important as the ClO radical in continuing the chain, when the pressures of Cl_2O and H_2 are comparable.

The decomposition of chlorine monoxide can be effected by the 5460A line in the presence of bromine as photosensitizer; under these conditions, the quantum yield is 4.3.[124]

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[119] Schumacher, H. J., and Wagner, C., *Z. physik. Chem.*, **5B**, 199 (1929).

[120] Goodeve, C. F., and Wallace, J., *Trans. Faraday Soc.*, **26**, 254 (1930), Finkelnburg, W., Schumacher, H. J., and Stieger, G., *Z. physik. Chem.*, **15B**, 127 (1931).

[121] Dickinson, R. G., and Jeffreys, C. E. P., *J. Am. Chem. Soc.*, **52**, 4288 (1930).

[122] Schumacher, H. J., and Townend, R. V., *Z. physik. Chem.*, **20B**, 375 (1933).

[123] Iredale, T., and Edwards, T. G., *J. Am. Chem. Soc.*, **59**, 761 (1937).

Chlorine Dioxide. Absorption bands of chlorine dioxide, beginning in the blue and violet regions[125] and extending to about 2700A, exhibit rotational fine structure only on the low-frequency side of 3750A.[126] At this point they begin to become diffuse because of predissociation. Schumacher believes a normal oxygen and ClO radical are produced and that at wave-lengths shorter than the convergence limit (2650A by extrapolation), the O atom is liberated in the excited state (^1D). Bowen reported the photodecomposition of the dioxide[127] to produce chlorine, oxygen and Cl_2O_6. Spinks, who secured similar products,[128] found light in the blue and ultraviolet regions equally effective for photodecomposition. Since chlorine dioxide does not absorb at 5460A, this wave-length is ineffective photochemically, except in the presence of bromine when a sensitized reaction occurs with a quantum efficiency practically equal to that produced by the 3650A line.

In later studies,[129] it was shown that in the presence of moisture the reaction is more regular than in the case of the dry gas. The quantum efficiencies for the moist gas are 3.7 at 3650A (predissociation region) and 3.1 at 4360A (excited molecule region). No atomic chlorine is formed. For low concentrations of chlorine dioxide the yield is independent of concentration and light intensity. In dry gas at 17°, the pressure decreases as Cl_2O_6 is formed and condenses on the walls.[130] The reaction is sensitive to temperature changes. At 30°, the pressure increases owing to the decomposition of Cl_2O_6 which yields chlorine and oxygen. In aqueous solutions, at concentrations of chlorine dioxide below 8 per cent, the rate of decomposition is proportional to the light intensity. In the solution there can be detected hypochlorite, chlorate and perchlorate ions.

PHOTOCHEMICAL REACTIONS OF CARBON COMPOUNDS

Photolysis of Carbon Dioxide. A 15-mm. layer of carbon dioxide at atmospheric pressure exhibits a series of absorption bands beginning at about 1710A (or somewhat longer wave-lengths); these apparently are superposed upon a continuum, possibly indicative of dissociation into carbon monoxide and oxygen.[131] Chapman, Chadwick and Ramsbottom[132] showed that after long intermittent illumination, dry carbon dioxide at atmospheric pressure was decomposed to the extent of 2.6 to 3 per cent. This decomposition was estimated by determining the ratio of carbon monoxide to carbon dioxide in the resulting gases. The oxygen was partially ozonized. When very carefully dried carbon dioxide was used, it was claimed that as much as 46 per cent could be decomposed in 45 hours. No decomposition whatever could be detected as a result of the irradiation of moist gas.

[124] Brown, A. G., and Spinks, J. W. T., *Canadian J. Research,* **15B**, 113 (1937).

[125] Mayer, H., *Z. physik. Chem.*, **113**, 220 (1924); Goodeve, C. F., and Stein, N. O., *Trans. Faraday Soc.*, **25**, 738 (1929); Goodeve, C. F., and Wallace, J., *Ibid.*, **26**, 259 (1930); Ku, Z. W., *Phys. Rev.*, **44**, 376 (1933).

[126] Urey, H. C., and Johnston, H., *Phys Rev.*, **38**, 2131 (1931); Schumacher, H. J., and Finkelnburg, W., *Z. physik. Chem. Bodenstein Band*, 704 (1931).

[127] Bowen, E. J., *J. Chem. Soc.*, **123**, 2328 (1923); Booth, H., and Bowen, E. J., *J. Chem. Soc.*, **127**, 510 (1925).

[128] Spinks, J. W. T., *J. Am. Chem. Soc.*, **54**, 1689 (1932); **55**, 428 (1933).

[129] Spinks, J. W. T., and Porter, J. M., *J. Am. Chem. Soc.*, **56**, 264 (1934).

[130] See also Bodenstein, M., Harteck, P., and Padelt, E., *Z. anorg. Chem.*, **147**, 233 (1925).

[131] Leifson, S. W., *Astrophys. J.*, **63**, 82 (1926).

[132] Chapman, D. L., Chadwick, S., and Ramsbottom, J. E., *J. Chem. Soc.*, **91**, 942 (1907); **89** 22 (1906).

The effect of water upon the reaction was verified by Coehn and Sieper.[133] The water underwent no change and neither formic acid nor formaldehyde was formed. It was also observed that the photolysis of dry carbon dioxide by radiations shorter than 2540A occurs at a rate inversely proportional to the pressure. A final stationary state is eventually reached. These authors claimed also that some formaldehyde is produced during the irradiation of a mixture of equal volumes of carbon dioxide and hydrogen.

More recently, Coehn and Spitta[134] confirmed and extended the observations on the effect of water upon photolysis of carbon dioxide. They concluded that optimum decomposition at a pressure of 300 mm. occurs in the presence of a very small proportion of water; the addition of larger quantities of moisture or further drying was believed to reduce the decomposition. These conclusions were based upon the observation that 1 per cent decomposition occurred in a sample dried over sulfuric acid, but that a gas which had been in prolonged contact with phosphorus pentoxide was not altered on irradiation. Drying by liquid air reduced the decomposition to 1 per cent but in this gas the addition of a very small quantity of moisture and subsequent ultraviolet irradiation produced a decomposition of 10.5 per cent. Coehn and May[135] have more recently confirmed the inability of ultraviolet light to cause a decomposition in extremely dry carbon dioxide. The xenon lamp decomposes carbon dioxide with a quantum yield of 0.98.[136]

It has been stated by Zenghalis[137] that the reduction of carbon dioxide in aqueous solution by very finely divided hydrogen takes place very slowly in the dark, but is markedly accelerated by sunlight and still more so by ultraviolet rays. In all cases the formaldehyde first produced undergoes polymerization.[137a]

Carbon Monoxide. Although the band spectrum of this gas has been much studied, its complexities are of little photochemical significance.[138] A series of bands extends from about 2064.5A to 920A. The absorption is but slight at wavelengths longer than 1546A. No continuous region is recorded since the heat of dissociation into normal atoms is too great for this process to occur in any readily available spectral region. There may be a predissociation limit at 1063A. Harteck, Groth and Faltings[139] find irradiation with the line 1295A (but not with 1470A) leads to the formation of carbon dioxide and carbon suboxide.

Thiele[140] observed that carbon monoxide and oxygen unite less readily under ultraviolet irradiation than do hydrogen and oxygen. Coehn and Tramm[141] reported that the presence of moisture has no effect on union of carbon monoxide and oxygen. Exposure of moist and various dried mixtures to the radiations from a quartz mercury arc led to practically the same result, combination occurring to the extent of 4 or 5 per cent within an hour. There was, however, some effect of moisture upon the degree of explosibility of the gas mixtures when treated by a spark. A moist mixture could be exploded by a spark at any pressure. A

[133] Coehn, A , and Sieper, G., *Z. physik. Chem.*, **91**, 347 (1916).

[134] Coehn, A., and Spitta, T., *Z. physik. Chem.*, **9B**, 401 (1930).

[135] Coehn, A., and May, B. W., *Z. physik. Chem.*, **26B**, 117 (1934).

[136] Groth, W., *Z. physik. Chem.*, **37B**, 307, 315 (1937).

[137] Zenghalis, C. D., *Compt. rend.*, **171**, 167 (1920); *J. Soc. Chem. Ind.*, **39**, 596A (1920).

[137a] For the sensitized reaction between carbon dioxide and water, see Chapter 43.

[138] Birge, R. T., and Hopfield, J. J., *Phys. Rev.*, **29**, 922 (1927); Leifson, S. W., *Astrophys. J.*, **63**, 82 (1926); Duffendack, O. S., and Fox, G. W., *Nature*, **118**, 12 (1926), Johnson, R. C., *Nature*, **118**, 50 (1926); Coster, D., and Brons, F., *Physica*, **1**, 155 (1934); Schmid, R., *Physik. Z.*, **37**, 55 (1936).

[139] Harteck, P., Groth, W., and Faltings, K., *Z. Elektrochem.*, **44**, 621 (1938).

[140] Thiele, H., *Z. angew. Chem.*, **22**, 2472 (1909).

[141] Coehn, A., and Tramm, H., *Ber.*, **54**, 1148 (1921).

mixture dried by short exposure to solid carbon dioxide and alcohol could not be exploded, but burned quietly. A mixture which had been cooled for a sufficient time could not be ignited, although a pale bluish zone appeared around the spark gap and slight combination was indicated by a small diminution in pressure.

An increase in the temperature coefficient with temperature was observed by Kistiakowsky.[142] This report and the fact that the gas mixture can be made to explode suggested to Jackson[143] that chain reactions are set up. The lack of absorption by carbon monoxide requires that the reaction produced by the 1720A line group of aluminum be explained by a primary dissociation of oxygen molecules. Since the yield of ozone was found to be about the same in mixtures of oxygen with either carbon monoxide or nitrogen, Jackson concluded that the efficiency of the process $O + CO \rightarrow CO_2$ must be at least 150 times lower than that of the reaction $O + O_2 \rightarrow O_3$. The activation energy of the first reaction is at least 3 kcal. greater than that of the latter, providing the steric factors influencing the efficiency of the collisions are the same in both cases. Harteck and Kopsch[144] have reported a similar unreactivity of oxygen atoms (from a discharge tube) toward carbon monoxide.

At high temperatures (500-550° C.), the dry oxidation of carbon monoxide is practically independent of temperature and total pressure. When water is present, the rate depends on the total pressure and has a large temperature coefficient. In the presence of water, the following chain may be set up, according to Jackson,

$$\begin{aligned} O + H_2O &\longrightarrow OH + OH \\ OH + CO &\longrightarrow CO_2 + H \\ H + O_2 + CO &\longrightarrow CO_2 + OH. \end{aligned}$$

The last two reactions had been suggested by Farkas, Haber and Harteck[145] to explain the photosensitizing action of ammonia in the oxidation of carbon monoxide. The primary photodissociation of the ammonia produces NH_2 and a hydrogen atom, the latter starting the last reaction. It has subsequently been found by Jackson[146] that at high temperatures, hydrogen peroxide is also formed in the presence of moisture.[147]

Popov[148] studied the oxidation of carbon monoxide at pressures as low as 0.01-1.5 mm. of mercury and at temperatures up to 150°. He found the reaction of carbon monoxide and atomic oxygen to be heterogeneous and to have a very small energy of activation. Contrary to the case of the oxidation of carbon monoxide by atomic oxygen obtained by means of a discharge, the efficiency of wall collisions was found to be large. This efficiency could be explained by assuming the participation of metastable ^1D oxygen atoms, which are obtained along with normal state atoms during the photodissociation of molecular oxygen. The reaction is then $CO_{ads.} + O' \rightarrow CO_2$ for the principal process. A correlation between the constants for the kinetic expression for this reaction and the isotherm of the adsorption of carbon monoxide on quartz could be shown.

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[142] Kistiakowsky, G. B., *Proc. Nat. Acad. Sci.*, **15**, 194 (1929).

[143] Jackson, W. F., *J. Am. Chem. Soc.*, **56**, 2631 (1934).

[144] Harteck, P., and Kopsch, U., *Z. physik. Chem.*, **12B**, 327 (1931).

[145] Farkas, L., Haber, F., and Harteck, P., *Naturwiss.*, **18**, 266 (1930); *Z. Elektrochem.*, **36**, 711 (1930).

[146] Jackson, W. F., *J. Am. Chem. Soc.*, **57**, 82 (1935).

[147] It has recently been claimed that the interposition of an oxygen filter does not affect the rate of the reaction, although a carbon monoxide filter decreases it. Ziskin, M., Kondrat'ev, V., and Sushkevitch, T., *J. Phys. Chem. (U.S.S.R.)*, **8**, 281 (1936); *Chem. Abs.*, **31**, 1297 (1937).

[148] Popov, B., *Acta Physicochim. U.R.S S.*, **3**, 223 (1935); *Chem. Abs.*, **30**, 2109 (1936).

The mercury-sensitized reaction between hydrogen and oxygen, in the presence of carbon monoxide, was studied by Barak and Taylor.[149] With equal concentrations of hydrogen and carbon monoxide, the former is oxidized five times as rapidly as the latter. When the hydrogen to carbon monoxide ratio was five to one, 20 per cent of the carbon monoxide formed formaldehyde. Reaction between hydrogen and carbon monoxide occurred at 18 per cent of the rate of that between hydrogen and oxygen in electrolytic gas. These results are consistent with an initial exclusive formation of hydrogen peroxide and a chain reaction with a mean chain-length of approximately six. In similar work, Farkas and Sachsse[150] found hydrogen atoms to combine with carbon monoxide molecules in three-body collisions to yield HCO. If the back reaction takes place and 0.1 of the three-body collisions are effective in the formation of the radical, the ratio of formation to decomposition at room temperatures is 1/370.

The phosgene-sensitized oxidation of carbon monoxide by the unfiltered radiations of the mercury arc has been investigated by Rollefson and Montgomery.[151] They gave the rate expression for low oxygen pressures as

$$\frac{d(CO_2)}{dt} = k\sqrt{I_0[\mathrm{COCl_2}][\mathrm{CO}][\mathrm{O_2}]}$$

At higher oxygen pressures, the rate becomes independent of the oxygen pressure. These authors suggested that the mechanism of this reaction is very similar to that of the chlorine-sensitized reaction.[152]

The latter is quite complicated, a thousand molecules of carbon dioxide per quantum being formed in mixtures of a half atmosphere each of chlorine, carbon monoxide and oxygen. In blue light at high pressures and in large vessels, the rate of production of carbon dioxide is proportional to the chlorine concentrations and to the square root of that of carbon monoxide. For small pressures and vessels with a large surface, it is proportional to the square root of the concentrations of carbon monoxide and chlorine.

In the presence of nitric oxide, a small proportion of the carbon monoxide present is, on irradiation by ultraviolet rays, converted into carbon dioxide by interaction with oxygen liberated from the nitric oxide.[153]

In the decomposition of carbon monoxide in the silent electric discharge a brown solid not identical with polymerized carbon suboxide is formed.[154]

THE PHOTOCHEMISTRY OF PHOSGENE

Formation of Phosgene. The formation of phosgene from carbon monoxide and chlorine, reported by Davy in 1812,[155] is somewhat analogous to the combination of hydrogen and chlorine in that the reaction has a very high quantum yield, is under certain conditions inhibited by oxygen and is to a high degree subject to the influence of traces of impurities which give rise to induction periods.[156]

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[149] Barak, M., and Taylor, H. S, *Trans. Faraday Soc.*, **28**, 569 (1932); for early observations see Herchefinkel, H., *Compt. rend.*, **149**, 395 (1909). See also page 257.

[150] Farkas, L., and Sachsse, H., *Z. physik. Chem*, **27B**, 111 (1934).

[151] Rollefson, G. K., and Montgomery, C. W., *J. Am. Chem. Soc.*, **55**, 4036 (1933)

[152] For a full discussion of the reaction schemes proposed for the latter, see Schumacher, H. J., and Stieger, G., [*Z. physik. Chem.*, **13B**, 157 (1931)]; Warming, E., [*Z. physik. Chem.*, **18B**, 153 (1932)]; Schumacher, H. J., [*Z. physik. Chem.*, **18B**, 155 (1932)]; and Franke, W. K., and Schumacher, H. J., [*Ibid.*, **B40**, 115 (1938)].

[153] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **157**, 129 (1913).

[154] Crespi, M., and Lunt, R. W., *J. Chem. Soc*, **127**, 2052 (1925); Lunt, R. W., and Mumford, L. S., *J. Chem. Soc.*, 1711 (**1929**).

[155] Davy, H., *Phil. Trans.*, **30**, 144 (1812).

Details of the kinetics of this reaction were reported by Bodenstein.[157] The results with various mixtures of carbon monoxide and chlorine were complicated and for a considerable time considered to be affected by traces of moisture present. It was established that oxygen retards the reaction until near completion of the latter, when its effect suddenly decreases. The oxygen is consumed by a chlorine-sensitized reaction in which carbon monoxide is oxidized to the dioxide. Carbon dioxide formation is proportional to the carbon monoxide pressure, increases with the chlorine pressure, but more slowly than in direct proportion, and decreases with increasing oxygen concentration, but not so rapidly as to be inversely proportional to the latter. At room temperature, the rate of formation of phosgene was found to be proportional to the chlorine concentration, to the square root of the absorbed energy and to the square root of the carbon monoxide concentration. The temperature coefficient near room temperature is unity or slightly less.

Subsequent work by Bodenstein and Onoda[158] revealed that the order of reaction is different at temperatures between 200° and 300°C. The rate of formation of the phosgene is then directly proportional to the absorbed energy, and to the concentrations of the reactants (chlorine and carbon monoxide). At these temperatures, furthermore, the retarding effect of oxygen is no longer observable. At 300°C. no formation of carbon dioxide occurs in the presence of oxygen. Between 270° and 300°C., the velocity coefficient is considerably influenced by hydrolysis of phosgene by water vapor, but at the higher temperatures all the water vapor appears to be removed in the early stages of the reaction. A poisoning effect of small quantities of carbon dioxide in the reaction at ordinary temperatures was demonstrated by Cathala.[159] The effect is diminished when wavelengths shorter than 3500A are employed in the irradiation.

As in the case of the hydrogen-bromine reaction, a mechanism to account for the kinetics of the reaction was developed by Bodenstein[160] by extending the mechanism used to account for the thermal reaction. The result was a succession of processes which involved excited chlorine and carbon monoxide molecules, as well as the chlorine atoms and triatomic chlorine molecules which are assumed to play a part in the thermal process. Although the introduction of a few assumptions regarding the rate constants of the partial reactions permitted a fairly satisfactory derivation of an expression similar to the experimental rate expression, the Bodenstein formulation has since been superseded by others which avoid the assumption of excited chlorine molecules as the products of the primary process.

A primary photodissociation of chlorine molecules was made the first step in the formulation of Bodenstein, Lenher and Wagner[161] which was based on an investigation of the reaction at low total pressures (below 40 mm.) and at ordinary temperatures. The partial reactions proposed were the following:

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[156] Chapman, D. L., and Gee, F. H., *J. Chem. Soc.*, **99**, 1726 (1911); Dyson, G., and Harden, A., *J. Chem. Soc.*, **83**, 201 (1903). For a general review, see Kistiakowsky, G. B., *Z. angew. Chem.*, **44**, 602 (1931). Early kinetic measurements were reported by Wildermann, M., *Phil. Trans.*, **199A**, 337 (1902); *Z. physik. Chem.*, **42**, 257 (1903).

[157] Bodenstein, M., *Rec. trav. Chim.*, **41**, 585 (1922).

[158] Bodenstein, M., and Onoda, T., *Z. physik. Chem.*, **131**, 153 (1928).

[159] Cathala, J., *J. chim. phys.*, **24**, 663 (1927).

[160] Bodenstein, M., *Sitzb. Preuss. Akad.*, **13**, 104 (1926); *Z. physik. Chem.*, **130**, 422 (1927); Schumacher, H. J., *Z. physik. Chem.*, **129**, 241 (1927).

[161] Bodenstein, M., Lenher, S., and Wagner, C., *Z. physik. Chem.*, **3B**, 459 (1929).

(1) $Cl_2 + h\nu \longrightarrow 2Cl$
(2) $CO + Cl \longrightarrow COCl$
(3) $COCl \longrightarrow CO + Cl$
(4) $CO + Cl_2 + Cl \longrightarrow COCl_2 + Cl$
(5) $COCl + Cl \longrightarrow CO + Cl_2$
(6) $COCl + O_2 \longrightarrow CO_2 + ClO$
(7) $ClO + CO \longrightarrow CO_2 + Cl.$

The last two reactions were employed only to account for the inhibiting action of oxygen and the sensitized formation of carbon dioxide. In this scheme there is supposed to be an equilibrium between the hypothetical COCl molecule and its decomposition products. The phosgene is formed only by the triple collisions in (4); it is to be noted that (4) is a chain reaction and accounts for the high quantum yield. By making the formation of phosgene depend upon a reaction involving triple collisions, the slowness of reaction at low pressures could be accounted for. In addition to processes (2) and (5), which represent removal of chlorine atoms in the gas phase, both COCl and Cl diffuse to the walls of the vessel where recombination occurs. Processes involving water were not included since Schultze[162] found the previously much-discussed effect of traces of moisture to be non-existent. By a treatment of these partial reactions in a manner analogous to that discussed in the section on hydrogen bromide, it can be shown that the rate constant is (as experimentally found) a function of the square root of the intensity of the light.

Lenher and Rollefson,[163] however, objected to the assumption of an equilibrium between COCl and CO and Cl on the ground that the hypothetical intermediate should be expected to react with chlorine as well as with oxygen. They assumed the phosgene to be formed by the process $COCl + Cl_2 \rightarrow COCl_2 + Cl$. Furthermore, the formation of the intermediate was believed to occur through a triple collision: $CO + Cl + M \rightarrow COCl$, in which chlorine molecules may function as the inert molecule with a relatively high efficiency. The rate of formation of phosgene was believed to be so fast compared to the rate of decomposition of COCl that the former may be considered the determining factor in fixing the concentration of the intermediate.

To account for the change in reaction order at 300°C. observed by Schumacher,[164] Lenher and Rollefson consider that the decomposition of COCl into Cl and CO is very rapid at this temperature. The equilibrium concentration of this intermediate (COCl) is very small, under which condition the chain-breaking reactions (6) and (7) have very small rates. The low steady state of COCl makes it necessary to assume for the formation of the phosgene reaction (4) of the Bodenstein, Lenher and Wagner mechanism. At room temperatures, reaction (4) is supposed to be subordinate to the process: $COCl + Cl_2 \rightarrow COCl_2 + Cl$. At high temperatures, chlorine atoms can only be removed by recombination at the wall or by collisions in the gas phase, rather than by combination with COCl. Therefore, the concentration of chlorine atoms becomes sufficient to permit of the formation of phosgene by the Bodenstein reaction. Schumacher and Stieger[165] showed that at temperatures above 250°C. and also at room temperatures when the total pressures were below one atmosphere or the vessels used had relatively large surfaces, a considerable portion of the chlorine atoms recombine on the walls of the vessel. The new mechanism is adequate to describe the rate of formation of phosgene under these conditions.

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[162] Schultze, G., *Z. physik. Chem.*, **5B**, 368 (1929).
[163] Lenher, S., and Rollefson, G. K., *J. Am. Chem. Soc.*, **52**, 500 (1930).
[164] Schumacher, H. J., *Z. physik. Chem.*, **129**, 241 (1927).
[165] Schumacher, H. J., and Stieger, G., *Z. physik. Chem.*, **13B**, 157 (1931).

Schumacher,[166] as well as Warming,[167] however, defended the mechanism of Bodenstein, Lenher and Wagner. They believe the rate of formation of COCl by triple collisions to be reasonably fast at ordinary pressures and state that the heat of formation of this molecule is so low that the decomposition must proceed at a rapid rate. Rollefson[168] asserts that it is impossible for COCl to attain its equilibrium concentration since other reactions, for example, between Cl_2 and COCl, occur too rapidly. The distinction is that in the Rollefson mechanism the COCl molecule may react either with chlorine or oxygen, the relative amounts of the two being determined by the specific rate constants and the relative pressures of the gases. On the other hand, in the Bodenstein mechanism it was postulated that only the oxygen could react with the COCl. The latter molecule was assumed to be in equilibrium with its dissociation products in the absence of oxygen, but not in its presence. The relative amounts of carbon dioxide and phosgene formed will depend upon the manner in which the COCl molecules divide between the two paths open to them. Increase of the pressure of oxygen at a definite pressure of chlorine should cause a decrease in the amount of phosgene formed and preliminary experiments appeared to indicate this to be the case. Rollefson[169] stated later that the specific rates for the two reactions destroying COCl are of the same order of magnitude. The phosgene formation has a higher temperature coefficient and therefore higher energy of activation than that leading to the formation of carbon dioxide. The relative amounts of the two reactions is a function solely of the ratio of chlorine to oxygen at constant temperature.

In a more recent paper, however, Rollefson[170] concludes that the active form of chlorine involved in the chain process is probably triatomic chlorine and believes the intermediate to be formed by

$$CO + Cl_3 \longrightarrow COCl + Cl_2.$$[171]

Recently, the reaction has been restudied by Bodenstein, Brenschede and Schumacher,[172] using very pure gases over a wide concentration range. The mercury line 4358A was used for the reaction at 14-16°C., pressure measurements being made with a quartz spiral manometer. Evidence was given to show that COCl rather than Cl_3 is the intermediate at chlorine pressures between 340 and 180 mm. Below this and down to 15 mm., there was evidence for an additional chain-breaking mechanism $H + COCl_2 \rightarrow HCl + COCl$ on the wall, and another method of phosgene formation. Also,[173] they have investigated the induction and after-periods by a rotating sector method, and found the resulting rate changes in agreement with those calculated from their mechanism. If the gases were not free from oxygen, the after-effects were five times as large. Oxygen inhibits the stationary formation of phosgene, but does not affect the equilibrium: $COCl \rightleftarrows CO + Cl$. This indicates the possible presence of an oxygen-containing intermediate compound with a longer life than either Cl or COCl.

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[166] Schumacher, H J., *J Am. Chem Soc*, **52,** 3132 (1930)

[167] Warming, E., *Z physik. Chem.*, **18B,** 156 (1932).

[168] Rollefson, G. K., *Trans. Faraday Soc*, **27,** 465 (1931).

[169] Rollefson, G. K., *J. Am. Chem. Soc.*, **55,** 148 (1933).

[170] Rollefson, G. K, *J. Am. Chem. Soc.* **56,** 579 (1934); see also Rollefson, G K., and Eyring, H., *J. Am. Chem. Soc.*, **54,** 170 (1932); Rollefson, G. K., *Z. physik. Chem.*, **37B, 472** (1937).

[171] Cathala, J., *J. chim. phys*, **25,** 182 (1928) had previously assumed the phosgene to be formed by the reaction: $Cl_3 + CO \rightarrow COCl_2 + Cl$

[172] Bodenstein, M., Brenschede, W., and Schumacher, H., *Z. physik. Chem.*, **28B,** 81 (1935); **40B,** 121 (1938).

[173] Bodenstein, M., Brenschede, W., and Schumacher, H. J, *Z. physik. Chem.*, **35B,** 382 (1937); See also Taylor, H. S., *J. Phys. Chem.*, **42,** 789 (1938).

The photochemical formation of phosgene from chloroform and oxygen (sensitized by chlorine) has been found to occur by Schumacher and Wolff.[174] The following mechanism is proposed:

$$
\begin{aligned}
&(1) \quad Cl_2 + h\nu \longrightarrow 2Cl \\
&(2) \quad Cl + CHCl_3 \longrightarrow CCl_3 + HCl \\
&(3) \quad CCl_3 + O_2 \longrightarrow CCl_3O_2
\end{aligned}
$$

The last compound forms phosgene and also breaks the chains. The quantum yield at 65° and a chloroform pressure of 100 mm. is 260 moles per einstein. The chain-breaking process can be neither a three-body collision nor diffusion to the walls since the rate is independent of the pressure. It is proportional to the absorbed light and to the square root of the chloroform concentration. The temperature coefficient is 1.23. The reaction is not influenced by hydrogen chloride or phosgene. It is almost completely inhibited by alcohols or ammonia, these substances being chlorinated and then decomposing. Completely chlorinated substances do not inhibit the reaction.[175]

Decomposition of Phosgene. Absorption data by Henri and Howell[176] indicated a region of absorption bands of phosgene to begin at 3041A. The bands become diffuse at 2750A and extend to 2380A beyond which the absorption becomes continuous. When phosgene is heated to 100-200°C., an additional continuous spectrum overlays the bands.

Weigert[177] found irradiation of phosgene at 500°C. caused no displacement from the thermal equilibrium ratio of the gas and its decomposition products, and in this Bodenstein and Onoda[178] concur. At the ordinary temperatures, phosgene, passed through a quartz tube at the rate of 1 cc. per minute, was decomposed to the extent of 3.3 to 4 per cent.[179] In a Uviol tube permeable only to radiations of wave-length longer than 2650A, the decomposition reached only 0.46-0.5 per cent. In ordinary glass tubes there was no decomposition. In each case the equilibrium could be approached from either side.

Almasy and Wagner-Jauregg[180] studied the decomposition of phosgene at 300 mm. pressure at both 20° and 160°C. in a quartz vessel surrounded by a mercury arc lamp. For isolating the region of bands a filter of 5 per cent benzene in hexane was used. To eliminate the effect of absorption by the liberated chlorine, the quartz vessel was surrounded by a chlorine filter. The contents of the vessel after irradiation were analyzed by freezing out the chlorine and phosgene and following the pressure change, or by titrating the chlorine and phosgene. The absorption of radiations in the region of sharp bands produced a decomposition to the extent of 0.25 to 1.75 per cent depending on the intensity of the light and the pressure of the phosgene. The decomposition was not increased at 160°C. It was assumed to be due to some process of predissociation and required no more han 100 kcal. The use of the entire mercury arc spectrum increased the decomposition to 2.19 to 8.65 per cent. Under these conditions the decomposition was nearly doubled at 160°C. Rollefson and Montgomery,[181] found that in the presence of oxygen, the rate of formation of carbon dioxide was directly proportional o the phosgene concentration and to the incident light intensity at either 20°, 90° or 200°C. At higher oxygen pressures, the rate was independent of the oxygen concentration, but at lower pressures it gradually fell off with decreasing oxygen, he rate being a function of the chlorine-oxygen ratio rather than of the oxygen concentration itself. They derived the rate law

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[174] Schumacher, H. J., and Wolff, K., *Z physik. Chem.*, **16B**, 453 (1934).

[175] Schumacher, H. J., and Sundhoff, D., *Z. physik. Chem*, **34B**, 300 (1936)

[176] Henri, V., and Howell, O. R, *Proc. Roy. Soc.*, **128**, 192 (1930).

[177] Weigert, F., *Ann. Physik*, **24**, 55 (1907).

[178] Bodenstein, M., and Onoda, T., *Z. physik. Chem.*, **131**, 153 (1928).

[179] Coehn, A., and Becker, H., *Ber.*, **43**, 130 (1910)

[180] Almasy, F., and Wagner-Jauregg, T., *Naturwiss.*, **19**, 270 (1931); *Z. physik. Chem.*, **19B**, 405 (1932).

$$\frac{d(CO_2)}{dt} = \frac{kI_0(COCl_2)}{1 + k'\left(\frac{Cl_2}{O_2}\right)}$$

rom the following series of reactions.

(1) $COCl_2 + h\nu \longrightarrow COCl + Cl$
(2) $COCl + O_2 \longrightarrow CO_2 + ClO$
(3) $COCl_2 + ClO \longrightarrow CO_2 + Cl_2 + Cl$
(4) $COCl + Cl_2 \longrightarrow COCl_2 + Cl$
(5) $Cl + M \longrightarrow 1/2Cl_2 + M$
(6) $Cl + Cl \longrightarrow Cl_2$

From the derivation it is apparent that the value of k' in the rate equation expressed he relative reactivity of the COCl molecule with chlorine and with oxygen. The average quantum yield of the decomposition was found to be 1.8. For the phosgene-sensitized oxidation of carbon monoxide they found quantum yields of 90 to 110, ower than those of others cited in the discussion of that reaction.[182]

The exposure of mixtures of phosgene and hydrogen to ultraviolet radiation results in a much greater decomposition, up to 97 per cent, since liberated chlorine may combine with the hydrogen to form hydrogen chloride. Bredig and von Goldberger [183] failed in attempts to obtain formaldehyde according to the reaction: $COCl_2 + 2H_2 \rightarrow CH_2O + 2HCl$. At 10°C., minute traces were obtained, but there was none at all at 80°C. The walls of the reaction vessel were observed to be coated with a white to brown deposit.

Montgomery and Rollefson [184] found the initial rate of the decomposition in the presence of hydrogen to be rather insensitive to a tenfold variation in the pressure of the latter gas, although the initial rate showed a slight increase as the hydrogen pressure was increased. With increase in the phosgene pressure, the rate had an upward trend but appeared to approach a limiting value at high phosgene pressures. By plotting the initial rates against the calculated percentage of absorption of the 2537A line (the most intense line beyond the predissociation limit) a straight line was obtained, indicating the rate to be a function of the first power of the absorbed light, as well as of the incident intensity. There was, however, a deviation from a simple first order law, since the rate of change of the logarithm of the phosgene concentration did not remain constant with time. In seeking the cause of this deviation, it was found that the rate is inversely proportional to, or at least involves a term which is inversely proportional to, the total pressure as varied by the addition of carbon dioxide or nitrogen. This effect was more pronounced when carbon monoxide was the added gas, in which case there was some evidence that the carbon monoxide concentration enters the rate law explicitly. It appeared likely that the deviation from first order may depend upon the ratio of added hydrogen to added carbon monoxide when both are added.

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[181] Rollefson, G. K., and Montgomery, C. W., *J. Am. Chem. Soc.*, **55**, 142 (1933).
[182] Montgomery, C. W., and Rollefson, G. K., *J. Am. Chem. Soc.*, **55**, 4025 (1933).
[183] Bredig, G., and v. Goldberger, A., *Z. physik. Chem.*, **110**, 521 (1924).
[184] Montgomery, C. W., and Rollefson, G. K., *J. Am. Chem. Soc.*, **55**, 4030 (1933).

From the reaction mechanism

$$\begin{array}{ll} (1) & COCl_2 + h\nu \longrightarrow COCl + Cl \\ (2) & Cl + H_2 \longrightarrow HCl + H \\ (3) & H + COCl_2 \longrightarrow CO + Cl + HCl \\ (4) & CO + M + Cl \longrightarrow COCl + M \\ (5) & 2COCl \longrightarrow COCl_2 + CO \end{array}$$

it was possible to derive the rate equation

$$\frac{d(CO)}{dt} = I_0(COCl_2)\left[1 + \frac{k_2(H_2)}{k_4(CO)(M)}\right]$$

which seemed in agreement with the experimental facts. The second term makes its largest contribution to the rate at the start of the reaction, and the first two or three values of the divergence from a first order reaction are always larger than succeeding values. It also appeared that the quantum yield was 3.7 at two minutes, decreasing to 2.4 at eight minutes. The concentration of M (any molecule capable of taking up the excess energy of COCl and so stabilizing it) was assumed equal to the total pressure. This would be the case if all kinds of molecules present are equally capable of acting in this way, even though carbon monoxide may have a more pronounced effect than nitrogen. The absence of formaldehyde formation was attributed to the non-reactivity of COCl toward hydrogen. This non-reactivity is believed to cause an increase in the concentration of COCl so that reaction (5) becomes the chain-terminating process.

Kassel[185] found an error in the derivation of the rate law in that the rate of production of CO in (5) was erroneously taken as equal to the rate of consumption of COCl in this step. If this is corrected, the 1 within the bracket of the final rate equation drops out and agreement with experiment is lost Kassel suggested the mechanism:

$$\begin{array}{ll} (3a) & H + COCl_2 \longrightarrow HCl + COCl \\ (5a) & 2COCl \longrightarrow 2CO + Cl_2 \\ (7) & COCl + Cl_2 \longrightarrow COCl_2 + Cl \\ (8) & COCl + H_2 \longrightarrow CO + HCl + H. \end{array}$$

This leads to the rate equation

$$\frac{d(CO)}{dt} = \frac{2I_{Abs}k_2(H_2)}{k_2(H_2) + k_4(CO)(M)} + k_8\sqrt{I_{Abs}/k_{5a}}(H_2)$$

Some work has been done on the photochemistry of bromophosgene. Trautz[186] had stated that the bromo compound could be formed photochemically. However, Schumacher and Bergmann,[187] who irradiated mixtures of carbon monoxide and bromine with different portions of the spectrum, concluded that at temperaures less than 100°C., neither excited bromine molecules nor bromine atoms react vith carbon monoxide to form bromophosgene. Furthermore, when mixtures of romophosgene and bromine were irradiated with light in the absorption band egion of bromine, no pressure change was noted. When irradiated in its own bsorption region (3200-2100A) bromophosgene is, however, decomposed with a uantum yield of unity. The reaction is of zero order and non-absorbing foreign ases do not affect the rate. The temperature coefficient is one for 10° between 0° and 40°C.

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[185] Kassel, L. S., *J. Am. Chem. Soc.*, **56**, 243 (1934)

[186] Trautz, M., *Z. Elektrochem.*, **21**, 329 (1915).

[187] Schumacher, H. J., and Bergmann, P., *Z. physik. Chem.*, **13B**, 269 (1931).

No reaction between carbon monoxide and fluorine could be detected when a nixture of these gases was irradiated in a quartz tube by ultraviolet rays.[188]

The Photochemistry of Nitrogen Compounds

The absorption by nitrogen has been studied by Birge and Hopfield[189] and y Sponer.[190] The spectrum consists of a system of bands beginning at 1450A nd extending to 1227A. Excited molecules are formed. No photochemical reacons which can be attributed to this absorption are known as yet.

Ammonia. The ultraviolet absorption of this gas is limited to the region f wave-lengths shorter than about 2200A or 2400A. Between this limit and 1860A ; a region of absorption with a maximum at 1910-1935A.[191] This region comrises a series of diffuse predissociation bands, the investigation of which by onhoeffer and Farkas[192] gave the first indication that predissociation in general nplies a spontaneous decomposition. These workers were unable to observe uorescence of light absorbed in this region, showing that the molecules excited y absorption did not persist long enough to emit energy spontaneously. By the se of the para-hydrogen method, Geib and Harteck[193] subsequently proved the resence of atomic hydrogen in ammonia which has absorbed radiations within iis region.[194] The primary process appears to be a dissociation into NH_2 and H; combination is rapid, and the concentration of hydrogen atoms is very small. urther spectroscopic evidence for this interpretation was found in the measureents and analysis by Dixon[195] of 16 strong bands between 1900 and 2400A. uncan[196] has shown that the diffuse predissociation bands continue to 1665A, ter which they become sharp and show rotational fine structure. True connuous absorption does not appear until about 1200A. At 1150A and below, the ntinuous absorption becomes so strong that the superposed sharp bands can no nger be measured accurately; the latter continue, however, at least down to)85A. Electron impact studies of ammonia at electron accelerations correspondg to wave-lengths within this very short wave-length region have been reported r Waldie,[197] Bartlett,[198] and McLennan and Greenwood[199] but are of little significance for the photochemistry of ammonia. Experiments on the decomposition of ammonia in discharge tubes[200] have also been indicative of the formation of atomic hydrogen and of some compound of hydrogen and nitrogen, NH_2 or NH.

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[188] Humiston, B., *J. Phys. Chem.*, **23**, 572 (1919); *Chem. Abs.*, **14**, 534 (1920).

[189] Birge, R. T., and Hopfield J. J., *Astrophys. J.*, **68**, 257 (1928); Hopfield, J. J., *Phys. Rev.*, **36**, 9 (1930).

[190] Sponer, H., *Proc. Nat. Acad. Sci.*, **13**, 100 (1927); *Z. Physik*, **41**, 611 (1927).

[191] Landsberg, G., and Predwoditeleff, A., *Z. Physik*, **31**, 544 (1925).

[192] Bonhoeffer, K. F., and Farkas, L., *Z. physik. Chem.*, **134**, 337 (1928).

[193] Geib, K. H., and Harteck, P., *Z. physik. Chem. Bodenstein Band*, 861 (**1931**).

[194] Ammonia is also known to sensitize reactions in which atomic hydrogen is required. Farkas, L., aber, F., and Harteck, P., *Naturwiss.*, **12**, 267 (1930); Taylor, H. S., and Emeléus, H. J., *J. Am. em. Soc.*, **53**, 562 (1931).

[195] Dixon, J. K., *Phys. Rev.*, **43**, 711 (1933).

[196] Duncan, A. B. F., *Phys. Rev.*, **47**, 822 (1935).

[197] Waldie, A. T., *J. Frank. Inst.*, **200**, 507 (1925).

[198] Bartlett, J. H., Jr., *Phys. Rev.*, **33**, 169 (1928).

[199] McLennan, J. C., and Greenwood, G., *Proc. Roy. Soc.*, **120A**, 283 (1928).

Chemical evidence for the decomposition of ammonia by ultraviolet light was first advanced by Regener[201] and by Berthelot and Gaudechon.[202] Coehn and Prigent[203] were unable to demonstrate a stationary state. Instead the decomposition appeared to go to completion within six hours. The ammonia was sealed in quartz tubes and irradiated with a quartz mercury arc. No ammonia could be demonstrated in a mixture of nitrogen and hydrogen, with or without chlorine as sensitizer, after irradiation with a quartz mercury arc. Noyes[204] has found ammonia to be formed in small amounts when a mixture of nitrogen, hydrogen and mercury vapor is exposed at the boiling point of mercury to light from a quartz mercury arc. Only traces of hydrazine could be detected. The reaction has been attributed to the dissociation of hydrogen by the excited mercury atom.[205]

The quantum yield of the decomposition of ammonia at room temperature by wave-lengths 2025 to 2041A was found by Warburg[206] to be 0.23-0.25. The rate of the decomposition was not affected by the addition of the decomposition products, even when so much of these were added as to make the ammonia but 5 per cent of the gas mixture. Kuhn[207] found the rate proportional to the incident light intensity, and verified the observation that the quantum yield was independent of the ammonia pressure. The value of the yield was, however, 0.45, nearly twice that of Warburg. The yield could, however, be decreased to 0.10 by using light of only two spectral lines, 2063 and 2100A. At high temperatures (500°C.) the speed of decomposition was nine times as great as at 20°C. The quantum yield increased by about 50 per cent for every 100° increase in temperature, reaching 3.3 at 500°. At this temperature the rate of decomposition could be retarded by the addition of hydrogen, although nitrogen had no effect.

In a repetition of these experiments, Wiig and Kistiakowsky[208] verified the Warburg values for the quantum yield at room temperature, 0 23, zinc spark, mean wave-length, 2090A, 0.24, aluminum spark, mean wave-length, 1962A, 0.25, cadmium spark, mean wave-length, 2144A. At 500°C. the quantum yield increased only to 0.48. They were inclined to attribute Kuhn's high value at 500°C. and his observation of a decrease in quantum yield when the monochromatic nature of the light was increased, to experimental error. They found further that the quantum yield is independent of the ammonia pressure over the range 1 to 800 mm. Also the quantum yield was not affected by seven fold variations in the intensity of the radiation or of seventeen-fold variations in the extent to which decomposition had occurred when the data were taken for the computations.

The use of radiations transmitted by fluorite but not by quartz increases the quantum yield to 0.69, so that the yield appears to be higher in the region 1900-1600A.[209] The xenon lamp, however, gives a quantum yield of but 0.17.[210]

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[200] Hutchinson, W. K., and Hinshelwood, C. N, *Proc Roy. Soc*, **117A**, 131 (1927); Lavin, G. I., and Bates, J. R., *Nature*, **125**, 709 (1930).

[201] Regener, E., *Preuss. Akad*, 1228 (1904)

[202] Berthelot, D., and Gaudechon, H, *Compt. rend*, **150**, 1169, 1327, 1517, 1690 (1910); **155**, 207 (1912); **156**, 124 (1913).

[203] Coehn, A., and Prigent, G., *Z. Elektrochem.*, **20**, 275 (1914).

[204] Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **47**, 1003 (1925).

[205] For the synthesis of ammonia in an arc, see Storch, H. H., and Olson, A R., *J. Am. Chem. Soc*, **45**, 1605 (1923); Olson, A. R., *Ibid.*, **48**, 1298 (1926); Mochan, I., Roginskiĭ, S., Fedorov, F., and Shekhter, A., *Compt. rend. acad. sci. (U.R.S.S.)*, **2**, 365 (1934); *Chem. Abs.*, **28**, 5339 (1934).

[206] Warburg, E., *Sitzb. Preuss. Akad.*, 746 (1911); 216 (1912); 872 (1914).

[207] Kuhn, W., *Compt. rend.*, **178** (1924); **177**, 956 (1923); *J. chim. phys.*, **23**, 521 (1926).

[208] Wiig, E. O., and Kistiakowsky, G. B., *J. Am Chem Soc.*, **54**, 1806 (1932).

Prior to the work of Bonhoeffer and Farkas on the nature of the predissociation process, evidence was advanced by both Dickinson and Mitchell[211] and Taylor and Bates[212] that was difficult to reconcile with the simple excited molecule mechanisms. These workers showed that the decomposition mixture contained more hydrogen (87-96 per cent) than would correspond to the stoichiometrical relation. This could be interpreted only as indicative of the formation of some hydrazine. Bates and Taylor suggested that excited ammonia molecules might either react with normal molecules to produce hydrazine and ammonia or that they might spontaneously yield atomic hydrogen and NH_2 radicals, the latter then forming hydrazine and atomic hydrogen by reaction with ammonia, or reforming ammonia and atomic hydrogen by reacting with hydrogen molecules.

At present, the NH_2 molecules, which are responsible for the formation of hydrazine, are regarded as arising from the predissociation of ammonia. Not much hydrazine is formed when ammonia is irradiated at room temperatures. Wiig and Kistiakowsky even found the composition of the resulting gases to be the same as that formed in the thermal decomposition, that is, close to a 1:3 nitrogen: hydrogen ratio. Koenig and Brings[213] studied the formation of hydrazine at temperatures of −80°C. in the glow discharge, but found that the yield, referred to the electrical energy consumed, was smaller than that with flowing gas at room temperature. Irradiation by the zinc spark caused not only formation but also decomposition of hydrazine, so that only traces could be obtained. They believed hydrazine to be formed in larger amount by the reaction $NH_3 + NH \rightarrow N_2H_4$ than by direct combination of two NH_2 radicals. Gedye and Rideal[214] claimed the yield could be increased by employing low temperatures, a high rate of gas flow and rapid cooling of the gaseous decomposition products. Under the best conditions and using the entire mercury arc spectrum, the yield of hydrazine was said to amount to 50 per cent of the ammonia decomposed.

Wiig and Kistiakowsky discounted the dissociation of ammonia into NH and H_2, since such dissociation did not lead to a mechanism in agreement with the experimental results.[215] Nor did they believe their failure to observe hydrazine in the ammonia decomposition could be ascribed to its simultaneous photochemical decomposition.[215a] They considered the likelihood of occurrence of each of the following secondary reactions.

(1) $H + H + M \longrightarrow H_2 + M$
(2) $NH_2 + H + M \longrightarrow NH_3 + M$
(3) $NH_2 + H_2 \longrightarrow NH_3 + H$
(4) $NH_3 + H \longrightarrow NH_2 + H_2$
(5) $NH_2 + NH_2 + M \longrightarrow N_2H_4 + M$
(6) $NH_2 + NH_2 \longrightarrow N_2 + 2H_2$
(7) $N_2H_4 + H \longrightarrow N_2H_3 + H_2$
(8) $N_2H_3 + N_2H_3 \longrightarrow 2NH_3 + N_2$

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[209] Kassel, L. S., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **49**, 2495 (1927).

[210] Groth, W., *Z. physik. Chem.*, **37B**, 307 (1937).

[211] Dickinson, R. G., and Mitchell, A. G., *Proc. Nat. Acad. Sci.*, **12**, 692 (1926); *J. Am. Chem. Soc.* **49**, 1478 (1927).

[212] Taylor, H. S., and Bates, J. R., *Proc. Nat. Acad. Sci.*, **12**, 714 (1926).

[213] Koenig, A., and Brings, T., *Z. physik. Chem.*, *Bodenstein-Band*, 541 (1931)

[214] Gedye, G. R., and Rideal, E. K., *J. Chem. Soc.*, 1160 (1932).

[215] Wiig, E. O., and Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **54**, 1817 (1932).

[215a] See in this connection, the discussion of the photochemical decomposition of hydrazine.

Triple collisions are probably not necessary in reactions (2) and (5).[216] At room temperature, (3) may be neglected as it implies a retardation of the rate of decomposition by hydrogen, an effect observable only at high temperatures. According to Boehm and Bonhoeffer,[217] (4) occurs extremely slowly. It may be that the increase in the quantum yield at high temperatures can be accounted for by this reaction, and that (3) also becomes effective under these conditions. Reactions (7) and (8) were set up to explain the absence of more than traces of hydrazine. The reaction at ordinary temperatures involves, according to Wiig and Kistiakowsky, reactions (1), (2), (5) and (7). The quantum yield on these assumptions would be determined by the ratio k_2^2/k_1k_5, this fraction being required to have a value of eight in order to account for a quantum yield of 0.25.

By using deuterium as an indicator, Taylor and Jungers[218] concluded that reaction (2) occurs to such an extent as to make it one of the reasons for the low quantum yield.[219] By irradiating mixtures of ammonia and deuterium, an equilibrium mixture of NHD_2 and NH_2D were obtained.

Studies of the concentrations[220] of atomic hydrogen produced by the irradiation of ammonia showed that the yields were independent of the total pressure when the latter was varied from 250 to 760 mm. The atomic hydrogen was proportional to the 0.69 power of the absorbed light intensity, and passed through a maximum with increasing ammonia pressure. The effect of changing the temperature indicated that the reactions which destroy hydrogen atoms must have but an insignificant heat of activation. To account for their observations, they suggested that hydrogen atoms react with ammonia to form NH_4 molecules, decomposition of the latter at temperatures above 300°C. shifting the equilibrium to the left. At small ammonia pressures, the establishment of equilibrium was prevented by the diffusion of hydrogen atoms to the wall. Two reactions were accordingly suggested to account for the low quantum yield in the ammonia decomposition, $NH_4 + NH_2 \rightarrow 2NH_3$ and $NH_4 + NH_2 \rightarrow NH_3 + NH + H_2$, the first being three hundred times as probable as the second. The rise of the quantum yield observed to occur at temperatures over 400°C. may be due to the above equilibrium moving so far to the left that not sufficient NH_4 remains to produce ammonia by either of these reactions.

Recently, the range of ammonia pressures over which the quantum yield is independent of the ammonia pressure has been extended to cover pressures of 1.2 to 8.5 atmospheres.[221] The yield is also independent of wave-length. The value found (0.14) was, however, lower than that of other investigators. A rather rapid increase of quantum yield with temperature was found, the values being 0.34 at 250°C and 0.54 at 400°C., a result intermediate between those of Kuhn and of Wiig and Kistiakowsky. The method suggested for the disappearance of hydrazine assumed the reactions $H + N_2H_4 \rightarrow NH_3 + NH_2$ and $2NH_2 + N_2H_4 \rightarrow 2NH_3 + N_2 + H_2$. The former was regarded as the more probable.[222] The decomposition of hydrazine was regarded as a photochemical process sensitized by ammonia.

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[216] Mund, W., and van Tiggelen, A., *Bull. Soc. Chim. Belg*, **46**, 104, 227 (1937), *Ann Soc. Sci. Bruxelles*, Ser. I, 57, 92 (1937); *Chem. Abs.*, **31**, 5685, 6560, 6971 (1937) These authors devise a mechanism which avoids reaction (2). See also Mund, W, Brenard, G., and Kaertkemeyer, L., *Bull. Soc. Chim. Belg.*, **46**, 211 (1937). For a further discussion of these relatively inaccessible papers, see Taylor, H. S., *J. Phys. Chem.*, **42**, 783 (1938).

[217] Boehm, E., and Bonhoeffer, K. F., *Z. physik. Chem.*, **119**, 385 (1926); Taylor, H. S., and Jungers, J. C., *J. Chem. Physics*, **2**, 452 (1934).

[218] Taylor, H. S., and Jungers, J. C., *J. Chem. Physics*, **2**, 452 (1934).

[219] A similar conclusion was reached by Melville, H. W., from work on the mercury sensitized reaction [*Trans. Faraday Soc.*, **28**, 885 (1932)].

[220] Farkas, L., and Harteck, P., *Z. physik. Chem.*, **25B**, 257 (1934).

[221] Ogg, R. A., Jr., Leighton, P. A, and Bergstrom, F. W., *J. Am Chem Soc.*, **56**, 318 (1934).

Wiig[223] finds that as the ammonia pressure is increased from zero the quantum yield at 2100A rises from about 0.1 to a maximum of about 0.3 at 65 to 120 mm. pressure and then gradually falls off to about 0.18 at 840 mm. The average value is about that of Warburg, 0.25. The results agree with those of Ogg, Leighton and Bergstrom. It was also observed[224] that the values depend to some extent upon the size of the reaction cell, decreasing in a cell of larger diameter. The reaction appears to become heterogeneous at ammonia pressures less than about 300 mm. and may be partly heterogeneous at higher pressures. Welge and Beckman[225] detected the formation of hydrazine during the early stages of the reaction. The non-condensible portions of the gases had higher proportions of hydrogen than 75 per cent. At this early stage of decomposition, effected by the 1990A line, the quantum yields averaged 0.87 and appeared to approach unity as a limit. The high quantum yields made it seem that recombination of the primarily formed NH_2 and H is not as important as had formerly appeared to be the case. A small amount of hydrazine may, however, be decomposed by hydrogen atoms with the formation of ammonia and nitrogen. The effect of the latter reaction becomes more exaggerated as the reaction proceeds.

During the early period of the investigation of the reaction of ammonia on irradiation considerable light was thrown upon it by studies on the mercury-sensitized reaction.[226] It was, for example, in the case of the mercury-sensitized reaction that Taylor and Bates[227] observed the reaction products to contain 89 per cent of hydrogen and 11 per cent of nitrogen, a circumstance which led to the development of mechanisms permitting the formation of hydrazine. Dickinson and Mitchell,[228] who obtained 70 mole per cent of hydrogen, found the presence of argon and nitrogen at 0.3 mm. pressure had little effect on the reaction rate. On the other hand, hydrogen at 0.3 mm. and lower pressures had a large inhibiting effect, which increased with increasing ammonia pressures. Melville[229] observed that in the presence of mercury vapor and hydrogen, the decomposition was less rapid when the ammonia was irradiated simultaneously by a mercury arc and a zinc spark than when irradiated by the zinc spark alone. The mercury resonance line dissociates the hydrogen. The resulting hydrogen atoms were believed to recombine with the NH_2 groups (formed by the predissociation of the ammonia by the zinc lines) more rapidly owing to the higher partial pressure of hydrogen atoms under these conditions. Gedye and Rideal[230] found but little hydrazine produced in the mercury-sensitized reaction. The following mechanism is proposed by Welge and Beckman.[231]

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[222] See Dixon, J. K., *J. Am. Chem. Soc.*, **54**, 4262 (1932), and Wenner, R. R., and Beckman, A. O., *Ibid.*, **54**, 2787 (1932).

[223] Wiig, E. O., *J. Am. Chem. Soc.*, **57**, 1559 (1935).

[224] Wiig, E. O., *J. Am. Chem. Soc.*, **59**, 827 (1937).

[225] Welge, H. J., and Beckman, A. O., *J. Am. Chem. Soc.*, **58**, 2462 (1936).

[226] Dickinson, R. G., and Mitchell, A. G., *Proc. Nat. Acad. Sci.*, **12**, 692 (1926).

[227] Taylor, H. S, and Bates, J. R., *Proc. Nat. Acad. Sci.*, **12**, 714 (1926).

[228] Dickinson, R. G, and Mitchell, A. C. G., *J. Am. Chem. Soc.*, **49**, 1478 (1927).

[229] Melville, H. W., *Trans. Faraday Soc.*, **28**, 885 (1932).

[230] Gedye, G R., and Rideal, E. K., *J. Chem. Soc.*, 1160 (1932).

[231] Welge, H. J., and Beckman, A. O., *J. Am. Chem. Soc.*, **58**, 2462 (1936).

$$\begin{aligned}&Hg + h\nu \longrightarrow Hg'\\&Hg' + NH_3 \longrightarrow NH_3' + Hg\\&NH_3' \longrightarrow NH_3 + h\nu_3\\&NH_3' \longrightarrow NH_2 + H\end{aligned}$$

The low quantum yield of 0.12 was attributed to the occurrence of the fluorescence reaction.

Rate expressions were derived for this and the corresponding deuteroammonia (ND_3) reaction by Evans and Taylor.[232] Melville[233] suggests that the decompositions are brought about in collisions between ammonia or ND_3 and metastable atoms. The metastable atoms are produced from quenching collisions between $^3P_1$ atoms and ammonia or ND_3, the latter two being equally efficient. To account for the observed greater reactivity of ammonia, secondary reactions, unconnected with the mercury atom processes, were assumed. The quantum yield for the photosensitized reaction is about the same as that of the direct decomposition, so that the secondary reactions are the same.[234]

Berthelot and Gaudechon[235] exposed mixtures of ammonia and oxygen to the total radiation of the mercury arc and found nitrogen, hydrogen and water, but no nitrates or nitrites, as products of the reaction. The reaction produced by the 2080A line of the zinc spark was more complex, according to Bacon and Duncan,[236] since ammonium nitrate and smaller amounts of ammonium nitrite could be obtained. The process $NH_2 + O_2 \rightarrow NO + H_2O$ was assumed and the overall reaction could be written: $8NH_3 + 7O_2 \rightarrow 2N_2 + 2NH_4NO_3 + 8H_2O$.

The photochemical reaction of ammonia with carbon monoxide yields formamide as a primary product. The amide then undergoes secondary reactions.[237] Less than 5 per cent of the reacting ammonia yields hydrogen and nitrogen. The rate of ammonia decomposition approximately doubles in the presence of carbon monoxide. Methylamine and ethylamine also react with carbon monoxide, a much larger amount of gaseous decomposition products being formed than in the reaction of ammonia.

The Photochemical Decomposition of Hydrazine. Faint diffuse absorption bands (apparently predissociation bands) begin at about 2490A in 80 cm. layers of hydrazine vapor at 0.5 mm. pressure.[238] Continuous absorption begins at about 2370A (at 2260A in 20 cm. layers). Hilgendorff[239] gives the heat of dissociation as 122.4 kcal. per mole.

Elgin and Taylor found that radiations shorter than 2400A decompose hydrazine by the reaction: $2N_2H_4 \rightarrow 2NH_3 + N_2 + H_2$, the ammonia subsequently decomposing at a rate about one-tenth that of the hydrazine decomposition rate. The hydrazine decomposition rate is independent of temperature, and of the addition of nitrogen, hydrogen or ammonia. The reaction can also be sensitized to the 2537A mercury line by the addition of mercury vapor; in this case the rate of the hydrazine decomposition so greatly exceeds that of the ammonia (40 times) that a nearly complete separation of the two reactions is possible. Indeed, it is the most rapid reaction obtained by means of excited mercury. The rate of the sensitized reaction is 110-120 times the rate of the direct photochemical decomposition. It is a chain reaction, the quantum yield being about 13. The rate of the sensitized reaction also is unaffected by nitrogen, ammonia or hydrogen added separately, although apparently the addition of both hydrogen and ammonia retards the reaction rate. The lack of retardation by hydrogen alone is explained by the assumption that hydrogen atoms react with hydrazine. The rate of the sensitized reaction is directly proportional to the incident light intensity.

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[232] Evans, M. G., and Taylor, H. S., *J. Chem. Physics*, **2**, 732 (1934).

[233] Melville, H. W., *Proc. Roy. Soc.*, **152A**, 325 (1935).

[234] Farkas, L., and Melville, H. W., *Proc. Roy. Soc.*, **157A**, 621, 625 (1936); for the direct unsensitized decomposition of deuteroammonia, see Wiig, E. O., *J. Am. Chem. Soc.*, **59**, 955 (1937).

[235] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1327 (1910); see also Rakestraw, N. W., and Hollaender, A., *Science*, **84**, 442 (1936).

[236] Bacon, H. E., and Duncan, A. B. F., *J. Am. Chem. Soc.*, **56**, 336 (1934).

[237] Emeléus, H. J., *Trans. Faraday Soc.*, **28**, 89 (1932).

[238] Elgin, J. C., and Taylor, H. S., *J. Am. Chem. Soc.*, **51**, 2059 (1929); see also Imanishi, M., *Nature*, **127**, 782 (1931).

[239] Hilgendorff, H. J., *Z. Physik*, **95**, 781 (1935).

The observed facts regarding the direct photochemical reaction could be explained by the assumption of a primary process leading either to a dissociation into N_2H_3 and H or into two NH_2 radicals.

The quantum yields produced by monochromatic light of 1990A, were found by Wenner and Beckman[240] to range from 1.0 at a pressure of 2 mm. to 1.7 at 14 mm. The composition of the gases produced in the initial stages of the reaction was not in agreement with those reported by Elgin and Taylor. More hydrogen formed at the low hydrazine pressures than at the higher ones. The mechanism must differ from that of the mercury-sensitized reaction, because of the excess of hydrogen formed and because of the much lower quantum yield. Their suggested mechanism involved the reactions

$$\begin{aligned} &N_2H_4 + h\nu \longrightarrow N_2H_3 + H \\ &H + N_2H_4 \longrightarrow N_2H_3 + H_2 \\ &2N_2H_3 \longrightarrow 2NH_3 + N_2 \\ &2N_2H_3 \longrightarrow N_2 + H_2 + N_2H_4 \text{ (wall reaction).} \end{aligned}$$

The Decomposition of Hydrogen Azide. The ultraviolet irradiation of aqueous solutions of hydrogen azide yields mainly hydroxylamine and nitrogen with small amounts of ammonia and traces of hydrazine.[241] Gaseous hydrogen azide, on brief illumination with the 1990A line, gives a gas, non-condensable at liquid air temperatures; on longer illumination, a white solid, presumably ammonium azide, NH_4N_3, is formed.[242] Light absorption by gaseous hydrogen azide sets in at 2200A. The decomposition proceeds by two concurrent reactions, one yielding hydrogen and nitrogen, and the other ammonia and nitrogen.

$$2HN_3 \longrightarrow H_2 + 3N_2 \text{ and } 3HN_3 \longrightarrow NH_3 + 4N_2$$

Over a pressure range of two to 130 mm., three molecules are decomposed per absorbed quantum, when calculated to the formation of ammonia. When sensitized by mercury vapor, there are also two concurrent reactions during the early part of the run, although their relative extents differ from those observed in the unsensitized reaction.

During the early period of the photosensitized reaction, the ammonia formed reacts with excess hydrogen azide to form solid ammonium azide. When the pressure has reached a value 1.18 times its initial value, excess hydrogen azide has all been consumed. After this, ammonia formed by the decomposition of ammonium azide remains as a gas and results in a sudden increase in the rate of change of total pressure. As the decomposition nears completion, a new reaction

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[240] Wenner, R. R., and Beckman, A. O., *J. Am. Chem. Soc.*, **54**, 2787 (1932).

[241] Gleu, K., *Ber.*, **61**, 702 (1928).

[242] Beckman, A. O., and Dickinson, R. G., *J. Am. Chem. Soc.*, **50**, 1870 (1928); **52**, 124 (1930); Myers, A. E., and Beckman, A. O., *Ibid.*, **57**, 89 (1935).

$H_2 + HN_3 \rightarrow NH_3 + N_2$ becomes increasingly important. When the pressure becomes constant no hydrogen remains, and the end products are given by $3HN_3 \rightarrow NH_3 + 4N_2$.

The quantum yield of the photosensitized reaction in its initial stage is 3.6; at pressures below 2 mm. the yield decreases rapidly. The value is in agreement with a calculated value of 3.4 molecules of HN_3 decomposed by either reaction per quantum absorbed, calculated to the formation of ammonium azide. The following possible partial reactions may be written:

(1) $Hg + h\nu \longrightarrow Hg^*$

(2) $Hg^* + HN_3 \longrightarrow Hg + N_2 + HN$

(3) $HN + HN_3 \longrightarrow H_2 + 2N_2$

(4) $HN + HN_3 \longrightarrow N_2 + N_2H_2$

(5) $N_2H_2 + HN_3 \longrightarrow 2N_2 + NH_3$

(6) $NH_3HN_3 \longrightarrow NH_4N_3$ (*solid*).

18 per cent of the molecules react by (2) and (3) and 82 per cent by (2), (4), (5) and (6).

Reactions Involving the Oxides of Nitrogen. A direct combination of nitrogen and oxygen under the influence of rays from a quartz mercury arc occurs to a very slight extent.[243] Kondrat'ev[244] states that the amount of combination can be doubled by the addition of 5 per cent of hydrogen or of 28 per cent of carbon monoxide. The addition of both gases increases the yield ten times. It is assumed that excited oxygen molecules are involved in the combination process.

Nitrous Oxide. In the absorption spectrum of this gas there have been observed bands of nitric oxide. The presence of the latter is probably due to a photochemical decomposition occurring during the measurements.[245] Sen-Gupta[246] found that nitrous oxide absorbs light at 1850A, transmits better at about 1700A and absorbs again at 1580A. It was suggested that these absorptions represent dissociations into NO and nitrogen atoms in different metastable states. That produced by 1850A was said to be ^2D and that at 1580A ^2P. In each region the absorption is continuous.[247] Absorption begins at longer wave-lengths as the temperature is increased (2246A at 20°C. and 2604 at 675°C.). By plotting the wave-length of beginning absorption against temperature and extrapolating to 0°, (2140A) it was deduced that the minimum energy required for the dissociation into NO and N is 132 kcal. From studies on mixtures of nitrogen peroxide with nitrous oxide, Henriques, Duncan and Noyes[248] concluded that in the direct decomposition of the latter, a second primary process $N_2O + h\nu \rightarrow N_2 + O$ is also necessary to explain the observed quantum yields.

Macdonald[249] irradiated nitrous oxide at various pressures with radiations

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[243] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1517 (1910). They found also that nitrous and nitric oxides are each decomposed into their elements, some of each gas reacting with liberated oxygen to form higher oxides.

[244] Kondrat'ev, V., *Acta Physicochim. U.R.S.S.*, **3**, 247 (1935); *Chem. Abs.*, **30**, 6649 (1936).

[245] Lambrey, M., *Compt. rend.*, **186**, 1112 (1928).

[246] Sen-Gupta, P. K., *Proc. Roy. Soc.*, **146A**, 824 (1934); *Bull. Acad. Sci. United Provinces Agra Oudh, India*, **3**, 197 (1934); *Chem. Abs.*, **29**, 7806 (1935).

[247] Henry, L. A., *Compt rend.*, **200**, 656 (1935); *J. chim. phys.*, **32**, 437 (1935). See also Dutta, A. K., *Proc. Roy. Soc.*, **138A**, 84 (1932).

[248] Henriques, F. C., Jr., Duncan, A. B. F., and Noyes, W. A., Jr., *J. Chem. Physics*, **6**, 518 (1938).

[249] Macdonald, J. Y., *J. Chem. Soc.*, 1 (**1928**); *cf.* also Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **59**, 807 (1937).

(1860-1990A) from a condensed aluminum spark. The decomposition proceeded in accordance with the equation:

$$4N_2O \longrightarrow 2NO + O_2 + 3N_2.$$

The quantum efficiency was 3.9 and was fairly independent of the pressure (21 to 607 mm.) and temperature (0° to 40°).

Excited mercury atoms can bring about the decomposition.[250] In this case, nitrogen is liberated and the oxygen combines with the mercury, nitric oxide not being produced. The reaction velocity is proportional to the intensity of the 2537A line employed to excite the mercury.

A mercury-sensitized chain reaction between nitrous oxide and hydrogen has been studied by Melville.[251] Oxygen participates in both the making and breaking of the chains, the length of chains being approximately the same for the photochemical and the thermal reactions.

Nitric Oxide. Leifson[252] found an intense banded absorption to begin at 2264A. There are at least four groups of bands, which are interpreted as arising from combinations of four electronic levels with the ground state of the molecules.[253] No regions of continuous absorption are apparent.

Macdonald[254] found the decomposition produced by irradiating the gas with radiations of wave-lengths 1860-1990A to follow two courses. Ninety per cent of the decomposition yielded nitrogen and oxygen and 10 per cent followed the equation $3NO \rightarrow N_2O + NO_2$. The quantum efficiency in this case is given as 0.73. The data were interpreted in terms of a theory of excited molecules serving as intermediaries, since the spectral data did not indicate the nature of the bands to be suggestive of predissociation.

On the other hand, Flory and Johnston[255] have interpreted the primary process as one of predissociation, at least when the pressure was low (0.02 to 7 mm.). The final products of the reaction were found to be nitrogen and oxygen, the latter being partly destroyed by a reaction occurring when the gas was compressed in a McLeod gauge. In this process, a solid product presumably mercurous nitrate, was formed. It was shown that mercury[256] vapor in the apparatus from the gauge did not essentially affect the results and that the reaction was at least 98 per cent non-sensitized since the use of a mercury vapor filter failed to reduce the rate of decomposition. The use of a Blue-Purple Corex A filter which cuts off the radiation completely below 2300A, but shows 70 per cent transmission of the 2537A line, reduced the rate to 1.3 per cent of its value without the filter. A similar experiment with a Cellophane filter cutting out radiation below 2200A and transmitting 45 per cent of that of the 2537A line reduced the rate to about 1 per cent of that without the filter.[257]

The rate of decomposition was directly proportional to the rate of absorption of the effective wave-lengths. At very low pressures, the rate was also directly proportional to the pressure, a circumstance which eliminated an excited molecule mechanism. Were the primary process of the latter type, the rate would vary as the square of the pressure since collisions with normal molecules would be required to effect a decomposition of the excited molecules. Most of the reaction produced by the mercury arc was attributed to absorption of the 1832A line by the *delta* band of nitric oxide. Absorption of the 1849A line in the *beta* band may have a lesser effect which becomes significant at higher pressures in agreement with the rates observed at pressures above 3 mm. Sparks between aluminum, zinc, cadmium, nickel, copper and tin electrodes were effective to the same order of magnitude. The activity of such sparks was regarded as due primarily to absorption in the continuous background. That the process is one of predissociation finds some support in the work of Kaplan[258] on the emission bands of the gas. A calculated value for the molal heat of dissociation of nitric oxide, 121.95 kcal., is less than the energy of the 1830A line by 33.6 kcal. The dissociation products must, however, be normal atoms. The only secondary processes in the reaction are recombination processes occurring at the walls. It is suggested that at higher pressures the primary step may be predissociation from the upper levels of the *beta*-bands, rather than from the *delta*-bands.

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[250] Manning, W. M., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **54**, 3907 (1932).

[251] Melville, H. W., *Proc. Roy. Soc.*, **146A**, 737 (1934).

[252] Leifson, S. W., *Astrophys. J.*, **63**, 73 (1926).

[253] Sponer, H., and Hopfield, J. J., *Phys. Rev.*, **27**, 640 (1926); Jenkins, F. A., Barton, H. A., and Mulliken, R. S., *Phys. Rev.*, **30**, 150, 175 (1927); Lambrey, M., *Compt. rend.*, **186**, 1112 (1928); **187**, 210 (1928); **189**, 574 (1929); **190**, 261 (1930).

[254] Macdonald, J. Y., *J. Chem. Soc.*, 1 (1928).

[255] Flory, P., and Johnston, H., *J. Am. Chem. Soc.*, **57**, 2641 (1935).

[256] *Cf.* also Kondrat'ev, V., *Acta Physicochim. U.R.S.S.*, **3**, 247 (1935); *Chem. Abs.*, **30**, 6649 (1936).

[257] Under other conditions, however, Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **53**, 514 (1931) found good evidence for the existence of a mercury-sensitized reaction. Under his conditions, there was no direct reaction. The differences in the manner of operation of the mercury arc source were, however, such that the results of these observers may not have been contradictory.

Nitrogen Peroxide. At room temperatures this gas is composed of an equilibrium mixture of NO_2 and N_2O_4 molecules. The latter is non-absorbing in the visible range and the former is colored. Harris[259] found the single molecules to exhibit a banded absorption spectrum between 6000 and 2250A. Lambrey[260] tabulated the wave-lengths of the apparent absorption maxima and the individual intensities of the lines for the region 2083 to 4009A. The NO_2 molecule exhibits two limits of predissociation.[261] The first lies between 3800 and 3700A and the second between 2459 and 2200A. The diffuse bands of the first region extend to about 2596A, at which point they are suddenly replaced by a series of sharply defined bands probably coinciding with a different electronic transition. These bands then become diffuse at the second predissociation limit. The first limit corresponds to a dissociation into NO and a normal oxygen atom, the second to the production of an oxygen atom in the ^1D state.[262] The absorption attributed to the N_2O_4 molecules also present in the gas is continuous,[263] consisting of two broad structureless bands at about 3400 and 2400A.[264]

On irradiation by means of the mercury arc, nitrogen peroxide was found by Norrish[265] to exhibit a marked pressure increase. Since radiations transmitted by glass caused the pressure increase, the latter was attributed to a photochemical decomposition of the NO_2 molecules into nitric oxide and oxygen. The addition of either of these products completely reversed the reaction, nitric oxide being the more effective in displacing the equilibrium. The pressure increases rapidly at first, then slows down. The increase is complete in about fifteen minutes; when the illumination is stopped the pressure returns to its original value, rapidly at first and then more slowly. Constancy of pressure was attained when the rate of recombination of NO and oxygen became equal to the rate of the photodecomposition. Hydrogen had no effect on the increase of pressure. This work had been completed before the interpretation of the spectrum by Henri had appeared. Norrish, lacking this information, proposed a mechanism involving a reaction between an excited and a normal molecule of NO_2 in which molecular oxygen was produced.

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[258] Kaplan, J., *Phys. Rev.*, **37**, 1406 (1931).

[259] Harris, L., *Proc. Nat. Acad. Sci.*, **14**, 690 (1928).

[260] Lambrey, M., *Compt. rend.*, **188**, 251 (1929); see also Lambrey, M., and Corbière, J., *Compt. rend.*, **201**, 1334 (1935).

[261] Henri, V., *Nature*, **125**, 202 (1930).

[262] Mecke, R., *Z. physik. Chem.*, **7**, 127 (1930); Herzberg, G., *Z. physik. Chem.*, **10**, 189 (1930); Ionescu, A., *J. phys. radium*, **8**, 369 (1937).

[263] See also Carwile, L., *Astrophys. J.*, **67**, 184 (1928).

[264] *Cf.* Holmes, H. H., and Daniels, F., *J. Am. Chem. Soc.*, **56**, 630 (1934).

[265] Norrish, R. W. G., *J. Chem. Soc.*, 761 (1927).

By a method insuring only very low partial pressures of the reaction products, Dickinson and Baxter[266] were able to avoid the recombination of the products and the resulting heat effect. Under their conditions, it was not necessary to treat the reaction as an equilibrium and quantum yields could be determined for the direct decomposition. The yields were determined in a series of spectral regions, isolated by the use of filters. The following mean values, expressed as molecules of oxygen per quantum absorbed, were obtained: 4350A, 0.0046; 4050A, 0.036; 3660A, 0.77. At the low pressures used, the values were not markedly dependent on the pressure.

These observations were extended by Norrish[267] to include six wave-lengths. The yield was zero at 5760, 5460 and 4360A. For 4050A, it was 0.37, at 3650A 1.05 and for the range 3160 to 2650A, 1.04. It is particularly interesting that a photochemical threshold is found in the middle of a region in which the substrate absorbs strongly, the maximum absorption of nitrogen peroxide being at about 4500A where the quantum yield is zero. Light of the photochemically inactive wave-length 4360A produced an orange fluorescence and the violet light of 4050A, which is only partly effective photochemically, a much fainter greenish-yellow fluorescence. The spectra of the fluorescence at each wave-length possessed two wide maxima at about 6400 and 5900A, different intensity distributions accounting for the difference in color. At 3650A only a very faint fluorescence could be produced. When present, the fluorescence could be destroyed by the addition of oxygen. These observations can now be interpreted as evidence that predissociation begins at about the threshold region, necessitating a revision of previously assumed excited molecule mechanisms.

The presence of nitrogen pentoxide does not affect the decomposition of the nitrogen peroxide, according to Holmes and Daniels.[268] Their quantum yields, based on molecules of NO_2 decomposed, in a mixture of the above gases were 1.92 at 3130A, 1.83 at 3660A, 0.5 at 4050A and zero at 4360A. They also found that N_2O_4 is decomposed at 2650A with a quantum efficiency of 0.6. Although the lines 3660 and 3130A are absorbed by this gas, no measurable decomposition results. Helium, argon, nitrogen, oxygen, hydrogen, carbon dioxide and nitrous oxide were found to decrease the photolysis of NO_2, but were more effective in reducing fluorescence.

The synthesis of nitrogen dioxide in a glow discharge in a two to one oxygen:nitrogen mixture has been reported by Westhaver and Brewer.[269]

Nitrogen Pentoxide. The absorption of this gas, according to Urey, Dawsey and Rice[270] is continuous from 3050A into the Schumann region. The upper absorption limit corresponds with an energy of 93.2 kcal, suggesting that the primary reaction $N_2O_5 \rightarrow 2NO_2 + O$ occurs.

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[266] Dickinson, R. G., and Baxter, W. P., *J. Am. Chem. Soc.*, **50**, 774 (1928).

[267] Norrish, R. W. G., *J. Chem. Soc.*, 1158, 1604, 1611 (1929).

[268] Holmes, H. H., and Daniels, F., *J. Am. Chem. Soc.*, **56**, 630 (1934).

[269] Westhaver, J. W., and Brewer, A. K., *J. Phys. Chem.*, **34**, 554 (1930).

[270] Urey, H. C., Dawsey, L. H., and Rice, F. O., *J. Am. Chem. Soc.*, **51**, 3190 (1929). See also Jones, E. J., and Wulf, O. R., *J. Chem. Phys.*, **5**, 873 (1938).

Holmes and Daniels,[271] who also gave absorption data, stated that light of wave-lengths 2800 and 2650A decomposes the pentoxide with a quantum efficiency of 0.6.

Nitrogen pentoxide is also decomposed photochemically by blue light, but only in the presence of nitrogen peroxide as a sensitizer.[272] Light in the region 4000 to 4600A is responsible for the reaction, the rate being proportional to the energy absorbed by the nitrogen peroxide. At low concentrations of the sensitizer, the rate is proportional to the amount present. From the data given, Kistiakowsky [273] has calculated an upper quantum yield limit of about 18.

Fazel and Karrer [274] suggested that the excited nitrogen peroxide molecules transferred their energy by collisions of the second kind to molecules of nitrogen pentoxide, thereby dissociating the latter. Norrish,[275] however, suggested that the nitrogen peroxide might be decomposed, the resulting nitric oxide molecules then reacting with nitrogen pentoxide with the production of three molecules of nitrogen peroxide, the original sensitizer. Busse and Daniels [276] found the rate of this photosensitized reaction to be unaffected by collisions with oxygen, nitrogen or hydrogen. Bromine could not be substituted for the nitrogen peroxide even though the halogen has a rather similar absorption range. When added to a mixture containing nitrogen peroxide, bromine decreases the sensitizing efficiency of the latter, probably by absorbing a portion of the effective light. From measurements of the relative rates of decomposition of nitrogen pentoxide at 0°C. by radiations of wave-lengths 4350, 4050 and 3660A, and comparison with the data on the decomposition of nitrogen dioxide, Baxter and Dickinson [277] concluded the mechanism of the sensitized nitrogen pentoxide decomposition to be essentially that suggested by Norrish.

Nitrosyl Chloride. Magnanini [278] found nitrosyl chloride to exhibit weak absorption bands in the region 5300-6200A; strong absorption sets in at 5300A. Kistiakowsky [279] states that the absorption begins above 6300A and increases gradually toward the ultraviolet. In the region between 5100 and 4350A the banded structure showed faint but diffuse line structure. In the ultraviolet below the absorption maximum at 3300A no banded structure could be observed at all.

According to Kiss [280] visible light decomposes nitrosyl chloride incompletely into nitric oxide and chlorine, which recombine in the dark, a stationary state being finally reached. The temperature coefficient is unity (0° to 78°C.). Working with the spectral regions 4380-5000 and 4480-5200A, isolated by means of filters, Bowen and Sharp [281] found the quantum yield to be 0.5 independent of the extent of the decomposition. Their proposed mechanism included a primary dissociation into nitric oxide and a chlorine atom, followed by some secondary reactions in which the chlorine atom produced the transitory compound $NOCl_2$. Quite different results were reported by Kistiakowsky,[282] who obtained a quantum yield of 2.1 at each of several wave-lengths from 6350 to 4350A, and probably also at 3650A. No explanation could be given for the divergence from the results of Bowen and Sharp. Kistiakowsky also believed the spectral evidence favored an interpretation by means of excited nitrosyl chloride molecules rather than one of direct dissociation for the primary process.

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[271] Holmes, H. H., and Daniels, F., *J. Am. Chem. Soc.*, **56**, 630 (1934).

[272] Daniels, F., and Johnston, E. H., *J. Am Chem. Soc*, **43**, 72 (1921).

[273] Kistiakowsky, G. B., "Photochemical Processes," The Chemical Catalog Co, Inc., (Reinhold Publishing Corp.), New York, **1928**, 140.

[274] Fazel, C. S, and Karrer, S., *J. Am. Chem. Soc.*, **48**, 2837 (1926).

[275] Norrish, R. W. G., *Nature*, **119**, 123 (1927).

[276] Busse, W. F., and Daniels, F., *J. Am. Chem. Soc.*, **49**, 1257 (1927).

[277] Baxter, W. P., and Dickinson, R. G., *J. Am. Chem. Soc.*, **51**, 109 (1929).

[278] Magnanini, G., *Z. physik. Chem.*, **4**, 427 (1889).

[279] Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **52**, 102 (1930).

[280] Kiss, A., *Rec. trav. chim.*, **42**, 665 (1923).

[281] Bowen, E. J., and Sharp, J. F., *J. Chem. Soc.*, **127**, 1026 (1925).

Nitrogen Trichloride. The decomposition of nitrogen trichloride

$$2NCl_3 \longrightarrow N_2 + 3Cl_2$$

is sensitized by chlorine, the velocity being directly proportional to the light absorbed by the added chlorine.[283]

The reaction is of zero order with respect to nitrogen trichloride until the decomposition is practically complete; a semi-explosive reaction then occurs. With pressures of nitrogen trichloride of 0.146 to 2.48 mm. and of chlorine between 100 and 22 mm. the quantum efficiencies (at 4360 and 3650A) were high, between 17 and 5, depending on the pressure of the chlorine. They tended to approach a limiting value of about three at the highest pressures of chlorine. If the vessel is treated with water or heated to 100°C., the efficiency is abnormally high; the "maturing" of a vessel is chiefly the formation of an invisible film of ammonium chloride on the surface which indirectly establishes a constant condition of chain rupture in the gas phase. The relation between the yield and the chlorine pressure is given by

$$\frac{1}{0.0038P_{Cl_2}} = K_1$$

in which K_1 varies from 2.0 to 2.5 and is dependent on the size of the vessel. Foreign gases reduce the quantum yield to a limiting value of two, the relation being

$$\frac{1}{(0.0038P_{Cl_2} + K_2P_{Gas})} = 2.5.$$

The K_2 values were · helium 0.00093, argon 0.0016, nitrogen 0.0017, oxygen 0.0025 and carbon dioxide 0.0038. It was suggested that the added gas stabilizes by triple collisions an energy-rich complex, NCl_4, which is associated with the rupture of chains.

THE PHOTOCHEMISTRY OF SULFUR COMPOUNDS

The gaseous reaction between hydrogen and sulfur is greatly aided by the ultraviolet rays from a mercury vapor lamp, according to Norrish and Rideal.[284] The absorption spectrum of sulfur vapor contains a band with maximum absorption at 2750A according to Graham.[285] It is known that this value lies within one of the two predissociation regions possessed by sulfur vapor.[286]

The absorption of hydrogen sulfide, which is entirely continuous, begins at about 2800A and reaches a maximum at about 1850A.[287] The gas can be decomposed by the light of the mercury arc[288] or of the zinc spark. Using the latter source, Stein[289] found the quantum yield to be 2 (2050A) when the hydrogen sulfide pressure was 250 mm. At higher pressures the quantum yield reached 3.8. The nature of the primary process was not determined. On the other hand, Forbes, Cline and Bradshaw[290] find the yield to be unity and independent of pressure between 8 and 1400 mm. and of light flux over a 14-fold range at 2080A.

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[282] Kistiakowsky, G B., *loc cit.*

[283] Griffiths, J G A, and Norrish, R W. G, *Proc Roy. Soc*, **130A,** 591 (1931); **135A,** 69 (1932).

[284] Norrish, R W. G, and Rideal, E K., *J Chem Soc*, **125,** 2070 (1924); **123,** 3202 (1923).

[285] Graham, J. I., *J. Chem Soc.*, **98** (ii), 1015 (1910).

[286] Christy, A., and Naudé, S. M., *Phys. Rev.*, **37,** 903 (1931).

[287] Goodeve, C. F., and Stein, N. O., *Trans. Faraday Soc.*, **27,** 395 (1931).

The Oxides of Sulfur. Sulfur monoxide, spectral evidence for the existence of which has been presented by Henri and Wolff,[291] is said to undergo a photochemical decomposition when irradiated by the shorter ultraviolet wave-lengths.[292] A slight contraction in volume of sulfur dioxide was observed by Berthelot and Gaudechon[293] to occur in a sample of the gas irradiated over a mercury surface. Sulfur was deposited on the tube and the mercury became encrusted with a sulfate. Corresponding results were also obtained in the presence of oxygen. Similar observations have been reported by Hill,[294] who used a Uviol mercury lamp. He represented the decomposition as $3SO_2 \rightarrow 2SO_3 + S$. By interposing various filters it was found that the chief response is at 3130A, lying within the first absorption band of sulfur dioxide. The gas has a well-developed band system which extends from about 3400A to shorter wave-lengths.[295] Predissociation into SO and O sets in at about 1950-1900A. Predissociation also is possible at about 2100A.[296]

Kornfeld and McCaig[297] obtained the absorption spectrum of sulfur dioxide before and after it had been irradiated at low temperatures with an aluminum spark.

Although the gas decomposes at these wave-lengths into SO and O, the spectrum of SO was not observed. Because of its surplus vibrational energy, the latter was possibly consumed in an unexpectedly rapid reaction.

The spectrum of sulfur trioxide shows continuous absorption from 3300 to 2600A and from 2300 to 2000A.[298] Kornfeld[299] concludes that at 2760A dissociation produces SO_2 and a normal state oxygen atom.

Konstantinova-Shlezinger[300] states that the sulfur trioxide produced when sulfur dioxide is irradiated in a quartz vessel, is decomposed to some extent by the reaction $2SO_3 \rightarrow 2SO_2 + O_2$.

The Oxidation of Sulfur Dioxide. Coehn and Becker[301] found that the formation of sulfur trioxide proceeds fairly rapidly in a mixture of sulfur dioxide and oxygen in a quartz reaction vessel mounted within a mercury lamp. With a mixture of equal volumes of sulfur dioxide and oxygen, the content of sulfur trioxide was 65 per cent at equilibrium. The latter condition was attained within an hour at a temperature of 160°C. This is quite different from the thermal equilibrium, since in daylight at temperatures below 450°C., there is practically 100 per

[288] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1517 (1910).

[289] Stein, N. O., *Trans. Faraday Soc.*, **29**, 583 (1933).

[290] Forbes, G. S., Cline, J. E., and Bradshaw, B. C., *J. Am. Chem. Soc.*, **60**, 1431 (1938).

[291] Henri, V., and Wolff, F., *J. Phys. Radium*, **10**, 81 (1929).

[292] Cordes, H., and Schenk, P. W., *Trans. Faraday Soc.*, **30**, 31 (1934).

[293] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1517 (1910).

[294] Hill, R. A., *Trans. Faraday Soc.*, **20**, 107 (1924); see also Konstantinova-Shlezinger, M., *J. Phys. Chem. (U.S.S.R.)*, **6**, 601 (1935); *Chem. Abs.*, **29**, 7809 (1935).

[295] Watson, W. W., and Parker, A. E., *Phys. Rev.*, **37**, 1484 (1931); Henri, V., and Wolff, F., *J. Phys. Radium*, **10**, 81 (1929); Chow, T.-C., *Phys. Rev.*, **44**, 638 (1933); Wieland, K., *Nature*, **130**, 847 (1932); *Trans. Faraday Soc.*, **30**, 260 (1934).

[296] Franck, J., Sponer, H., and Teller, E., *Z. physik. Chem.*, **18B**, 88 (1932).

[297] Kornfeld, G., and McCaig, F., *Trans. Faraday Soc.*, **30**, 991 (1934); *Chem. Abs.*, **29**, 680 (1935).

[298] Dutta, A. H., *Proc. Roy. Soc.*, **137A**, 366 (1932).

[299] Kornfeld, G., *Trans. Faraday Soc.*, **33**, 614 (1937).

cent sulfur trioxide at equilibrium. The irradiation equilibrium was found not to be displaced by increases of temperature up to 800°C., whereas the dark equilibrium is displaced considerably when the temperature is raised above 450°C. The temperature coefficient of the oxidation rate was found to be 1.2. These authors also made experiments with flowing systems at temperature of 450°C. and obtained yields so high as to lead them to believe a technical process for the production of sulfuric acid to be feasible.[302]

In a repetition of this work, Trautz and Helfrich[303] found the mass law to hold within the limit of experimental error, and observed the equilibrium constant to vary linearly with the square of the current to the mercury arc. The introduction of argon or nitrogen had no effect on the equilibrium constant. They also claimed that completely dried sulfur dioxide neither decomposed when irradiated nor was oxidized in the presence of oxygen.

The quantum yields have been determined for a series of wave-lengths of monochromatic light by Kornfeld and Weegmann.[304] At 2537A and longer wave-lengths, the yield was less than 0.01, and even this was decreased by increasing the concentration of sulfur trioxide. The yields were 0.53 at 2200A, 0.71 at 2070A and 1.0 at 1806A. They attributed the results to a mechanism involving dissociation. The slight yields at the longer wave-lengths were said to be explained by a different mechanism since there is insufficient energy for dissociation. Franck, Sponer and Teller[305] considered the process of oxidation to involve excited molecules of sulfur dioxide. Beyond 1950A, in the predissociation region, they found the quantum yield to rise to three.

Sulfuryl Chloride. The absorption by this material is continuous at wave-lengths less than 2600A.[306] LeBlanc, Andrich and Kangro[307] stated the absorption to begin at 3000A and to rise rapidly at shorter wave-lengths. With radiations absorbed by sulfuryl chloride, but not to a marked extent by either sulfur dioxide or chlorine, there is practically complete dissociation either at 55°C. or at 100°C. These authors believed that irradiation of mixtures of sulfur dioxide and chlorine by wave-lengths absorbed by the former caused only slight changes which did not result in the formation of sulfuryl chloride. On the other hand, radiations absorbed by the chlorine caused the reaction to run to an equilibrium, the position of which depended on the temperature and the amount of moisture present.

Trautz[308] found that the radiations about 2900A caused the combination of the two gases to proceed smoothly as a second order reaction, particularly at higher temperatures. Sulfuryl chloride was not the only product of the reaction; if relatively short periods of exposure were separated by several hours of darkness, other substances formed and decreased the velocity constant. When continuous irradiation was employed, constants were no longer obtained, probably on account of the side reactions. A temperature increase of 80°C. decreased the velocity of the

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[300] Konstantinova-Shlezinger, M., *J. Phys. Chem. (U.S.S.R.)*, **6**, 601 (1935); *Chem. Abs.*, **29**, 7809 (1935).

[301] Coehn, A., and Becker, H., *Z. physik. Chem.*, **70**, 88 (1910).

[302] Coehn, A., and Becker, H., German P. 217,772, July 9, 1907.

[303] Trautz, M., and Helfrich, F., *Z. wiss. Phot.*, **33**, 72, 111, 117 (1934); *Brit. Chem. Abs.* **A**, 975, 1183 (1934).

[304] Kornfeld, G , and Weegmann, E , *Z. Elektrochem.*, **36**, 789 (1930).

[305] Franck, J., Sponer, H., and Teller, E., *Z. physik. Chem.*, **18B**, 88 (1932).

[306] Asundi, R. K., and Samuel, R., *Current Sci.*, **3**, 417 (1935); *Chem. Abs.*, **29**, 3914 (1935).

[307] LeBlanc, M., Andrich, K., and Kangro, W., *Z. Elektrochem.*, **25**, 229 (1919); *Chem. Abs.*, **14**, 493 (1920).

[308] Trautz, M., *Z. Elektrochem.*, **21**, 329 (1915).

combination, corresponding to a temperature coefficient of 0.88 per 10°C. The velocity of the formation reaction is of the same order as that which is catalyzed by animal charcoal in the dark, whether Uviol light or that from a quartz lamp is used.

Attempts to obtain sulfuryl bromide by the irradiation of sulfur dioxide and bromine have not been successful.[809]

Photochemistry of Miscellaneous Substances

Phosphine and Arsine. In the absorption spectrum of phosphine, Cheesman and Emeléus[810] observed poorly developed bands with centers at approximately 2315 and 2290A. Arsine and stibine showed only continuous absorption. In the photochemical decomposition of the latter, hydrogen was formed.

The mercury-sensitized decomposition of phosphine, as affected by variations in the partial pressures of phosphine, hydrogen, oxygen and argon, was investigated by Melville.[811] Collision of excited mercury atoms with phosphine was believed to produce H and PH_2. Recombination of these products by a wall reaction was indicated by the decrease in the reaction rate which was observed to follow an increase in the surface-to-volume ratio of the vessel. An observed inhibition by added hydrogen was attributed to the effect of the latter in deactivating the excited mercury atoms and to a wall reaction between the additional atomic hydrogen so produced and the phosphorus-containing intermediate. By attacking the intermediate, added oxygen increased the rate of the phosphine decomposition. That the oxide so formed initiated a stable chain reaction between the remaining phosphine and oxygen was shown by the acceleration of this reaction by argon.

The lowering of the explosion limit of phosphine-oxygen mixtures by mercury arc irradiation was shown to be due to a surface effect probably connected with the adsorption of hydrogen by the wall of the containing vessel. The direct photochemical decomposition of phosphine by the radiations from zinc or aluminum sparks leads to the formation of hydrogen and red phosphorus.[812]

Melville[813] also finds that at room temperature the absorption spectrum of phosphine consists of a region of continuous absorption beginning at 2300A, preceded by four diffuse bands. At 300°C., the bands disappear and the absorption limit moves toward longer wave-lengths. The direct photochemical decomposition has a quantum yield of 0.56 when conducted in a 7 cm. bulb and 0 49 in a 2 cm. bulb. It is independent of temperature below 300° Atomic, but not molecular, hydrogen decreases the yield.

An oxygen-phosphine mixture reacts explosively between two sharply defined pressure limits. The lower one can be diminished by irradiation between the wave-lengths of 2500 and 2800A. The effect is ascribed to the formation of a small quantity of an active substance from the phosphine; this does not decay immediately when the elimination ceases.[814]

Melville and Roxburgh[815] found for the reaction produced by irradiation of an oxygen-phosphine mixture at 0.05 mm. a quantum yield of 200, a stable chain reaction occurring. Above the upper limit of irradiation for explosion in the photochemical oxidation of phosphine, the chain reaction is inhibited by oxygen.

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[809] Trautz, M., *Z. Elektrochem.*, **21**, 329 (1915); Schwarz, R , and Kunzer, W., *Z. anal. Chem.*, **183**, 376 (1929).

[810] Cheesman, G. H., and Emeléus, H. J., *J. Chem. Soc.*, 2847 (1932).

[811] Melville, H. W., *Proc. Roy. Soc.*, **138A**, 374 (1932).

[812] Melville, H. W., *Nature*, **129**, 546 (1932).

[813] Melville, H. W , *Proc. Roy. Soc.*, **139A**, 541 (1933); Melville, H. W., and Bolland, J. L., [*Ibid.*, **160A**, 384 (1937)] and Melville, H. W., Bolland, J. L., and Roxburgh, L , [*Ibid* , 406] also investigated mercury-sensitized exchange reactions of deuterium and phosphine and the decomposition of trideuterophosphine.

[814] Hinshelwood, C. N., and Clusius, K., *Proc. Roy. Soc.*, **129A**, 589 (1930).

[815] Melville, H. W., and Roxburgh, L. H., *J. Chem. Physics*, **2**, 739 (1934).

Since the continuous absorption of arsine begins at only 2390A, the sensitized decomposition produced by mercury atoms excited by the 2537A line may be studied without any complication due to a direct reaction.[316] Hydrogen gas and a film of arsenic are formed. The rate of decomposition is directly proportional to the intensity of the light and, at high pressures, is independent of the arsine pressure. At low pressures, the rate is decreased because the excited mercury atoms lose some of their energy by fluorescence. The decomposition is very slightly inhibited by addition of hydrogen. The quantum yield is 1.03.

Germane absorbs only in the very short wave-length region, probably at about 1700A. Absorption is entirely continuous at least as far as 1550A.[317] Radiations transmitted by very thin layers of quartz will decompose germane into hydrogen and germanium. The primary process is uncertain. A mercury-sensitized reaction also leads to the same products.[318]

A mercury-sensitized decomposition of silane to hydrogen and a solid SiH_x has been reported by Emeléus and Stewart.[319] The lack of absorption by this material prevents the occurrence of any direct photochemical decomposition. Mixtures of 30-50 per cent of silane with oxygen at low pressures explode when irradiated by the mercury resonance line, hot mercury spark, or aluminum spark. The process may be due to the formation of excited oxygen molecules. At higher pressures (100-500 mm.), the mixture reacts slowly after an induction period which depends on the initial pressure and oxygen concentration to give silicon. At the beginning the pressure increase is an exponential function of the time.

Siloxene, $Si_6O_3H_6$, reacts with organic halides in the presence of light to produce a monohalogenated siloxene.[320] Siloxene absorbs only light of short wave-length, but can be sensitized to long wave-lengths by the addition of a very small quantity of hydroxysiloxene or of a dye. Since colored products are formed as the reaction proceeds, there is also autosensitization.

Iron pentacarbonyl vapor can be decomposed by irradiation with the wave-length 4000A, with a quantum efficiency of two.[321] The reaction is inhibited by foreign gases. Eyber explained the results by assuming an excited molecule to react with a normal one with the production of carbon monoxide and the compound $Fe_2(CO)_9$. On the other hand, Thompson and Garratt[322] found the vapor to have continuous absorption beginning at 4100A. They suggested that the primary process involves a dissociation into CO and $Fe(CO)_4$. The latter then reacts with a molecule of the pentacarbonyl to give the observed product $Fe_2(CO)_9$. In hexane or carbon tetrachloride the continuum began at 5500A, but this was attributed to the presence of the decomposition product as an impurity. Eyber found that hexane solutions absorb strongly below about 4600A.

Both the vapor and hexane or carbon tetrachloride solutions of nickel tetracarbonyl show only continuous absorption, beginning at 3950A. The first reaction of irradiation is to produce carbon monoxide and nickel tricarbonyl, the latter further dissociating into carbon monoxide and nickel. In the gas phase, however, no change is observed,[823] a thermal recombination balancing the photochemical decomposition. The quantum efficiency is higher, 2.12, for solutions in carbon tetrachloride than for those in hexane or cyclohexane. The yield increases somewhat with frequency from a threshold value corresponding to the limit of continuous absorption. Fedorov and Talmud[824] find the reaction can be sensitized to wave-lengths greater than 6400A by pinacyanol. Webster[825] claims the polymerization of nickel carbonyl to $(Ni(CO)_4)_2$, which has antiknock properties when added to motor fuels, by the action of actinic light.

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[316] Simmons, N. L., and Beckman, A., *J. Am. Chem Soc.*, **58**, 454 (1936).

[317] Mahncke, H. E., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **57**, 456 (1935).

[318] Romeyn, H., Jr., and Noyes, W. A , Jr , *J. Am. Chem. Soc* , **54**, 4143 (1932).

[319] Emeléus, H. J., and Stewart, K., *Trans. Faraday Soc.*, **32**, 1577 (1936). x is < 0.9. For disilane and trisilane decomposition, see Schwarz, R , and Heinrich, F., *Z. anorg allgem Chem.*, **221**, 277 (1935).

[320] Kautsky, H., and Thiele, H., *Z. anorg allgem. Chem.*, **144**, 197 (1925); *Chem. Abs.*, **19**, 2313 (1925).

[321] Eyber, G., *Z. physik. Chem.*, **144A**; see also Warburg, O , *Naturwiss.*, **16**, 856 (1928).

[322] Thompson, H. W., and Garratt, A. P., *J. Chem. Soc.*, 525 (**1934**).

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[823] Thompson, H. W., and Garratt, A. P., *J. Chem. Soc.*, 1817 (1934).

[824] Fedorov, F. P., and Talmud, D. L., *J. Phys. Chem. (U.S.S.R.)*, 8, 789 (1936); *Chem. Abs.*, 31, 1702 (1937).

[825] Webster, H. G., U. S. P. 2,002,805, May 28, 1935; *Chem Abs.*, 29, 4932 (1935).

Chapter 20

Inorganic Reactions in Liquids

GENERAL CHARACTERISTICS

In liquid phase reactions the photochemical mechanism may be altered because of the influence of neighboring molecules of the reactant if a pure liquid, or of the solvent if a solution, upon the molecule which absorbs a photon. These influences are exerted even during the act of absorption. As pointed out by Franck and Rabinowitsch,[1] the molecules in a liquid may be regarded as being permanently in a state of collision. As a result, collisions with adjacent molecules are occurring during the brief period between the absorption of a photon by a molecule and its dissociation (about 10^{-13} second). Such collisions may deactivate the excited molecule even before it has a chance to dissociate. Accordingly, the yield of the primary process might be expected to fall below unity. A lowered quantum yield in the primary process would be reflected also in a lowered quantum yield for the measured overall reaction. This consideration would apply to any photochemical process in which the primary act is the formation of an excited molecule.

Since all collisions between dissociation products would be triple collisions with solvent molecules, the occurrence of secondary recombination processes would be enhanced and contribute to a lowering of the quantum yield. Such processes would be true recombinations of the dissociation products of individual molecules rather than combinations of products of dissociation of different molecules or of products produced in secondary reactions. This follows because any excess kinetic energy with which atoms or free radicals may be endowed, by virtue of a dissociating photon of slightly shorter wave-length than corresponds to the energy required for dissociation, would be lost by collision before the products had moved much more than a molecular diameter. Recombination would then be possible if the products were still close together. When much shorter wave-lengths are used in irradiation, the kinetic energies of the dissociation products are great, enabling the latter to travel farther apart before losing this excess energy. The result would be a reduction of the chance of recombination and an increase in the quantum yield over that produced by the use of longer wave-lengths.[2]

In certain liquids and in solutions in non-polar solvents such as carbon tetrachloride, it is possible that the rates and temperature coefficients of secondary processes are not far different from those in the gaseous state.[3] In other cases there may be complications due to combinations of the solvent with the dissociation products of the primary process. Indeed, the original solute may be solvated and give rise to further complications. Details of effects exerted by the solvent upon secondary processes will be discussed in connection with individual reactions.

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[1] Franck, J., and Rabinowitsch, E., *Trans. Faraday Soc.*, **30**, 129 (1934).

[2] Sveshnikov, B. Y., [*Acta Physicochim. U.R.S.S.*, **3**, 257 (1935)] has discussed the theory of the quenching of the fluorescence of excited molecules as dependent on the viscosity of the solvent. He has also considered the effect the concentration of a reactant which does not require activation may have on the mean life of excited molecules. *Compt. rend. acad. sci. U.R.S.S.*, **15**, 177 (1937); *Chem. Abs.*, **31**, 656 (1938). Note also Schpolski, E., *Acta Physicochim. U.R.S.S.*, **3**, 255 (1935).

[3] Moelwyn-Hughes, E. A., "Kinetics of Reactions in Solution," p. 63. Oxford University Press, 1933.

Dickinson[4] pointed out that as a result of these possibilities, reactions in the liquid phase might be expected to have quantum yields less than, or in some cases equal to but never greater than, those of the same reactions in the gas phase. He examined the reactions in which available data permitted a comparison of the yields in the two states. Of eleven reactions studied, ten exhibited yields in the liquid phase which were slightly less than those in the gas phase. An exception was the decomposition of ethyl iodide produced by absorption within the continuous spectral region. This halide, according to West and Ginsburg,[5] undergoes little decomposition in the gas phase and more in the liquid phase or in solution in hexane or benzene. Dickinson, however, raised the question as to whether the effects of traces of oxygen had been entirely eliminated in this work.[6]

Rollefson[7] has discussed cases in which the solute is affected by the solvent and, in particular, the influence of the solvent, especially if polar, upon photosensitization processes effected by such fluorescent substances as uranyl salts.

Absorption Spectra. Spectral evidence as to the nature of the primary process—dissociation, predissociation or formation of excited molecules—is rarely available for the interpretation of photochemical reactions in condensed systems. However, the products capable of secondary reactions will be dissociation products, for collisions would easily lead to the dissociation of excited molecules. The absorption spectra of liquids seldom exhibit the fine structure characteristic of transitions between rotational levels of molecules seen in the absorption of gases and the occurrence of which was used as a criterion of the absence of predissociation. Even the more widely separated bands characterizing the vibrational levels of molecules are usually but partially distinguishable. The blurring of the finer structure is in part attributable to the effect of collisions with neighboring molecules and in part to the Stark effect of the charges of the adjacent molecules. The effects of collision-broadening may be lessened by making the observations at liquid air temperatures in some cases. This is particularly to be observed in the case of crystals. For example, at very low temperatures (20°Abs.) sharp lines replace the broad absorption bands of potassium dichromate observable at ordinary temperatures.[8]

In other cases, as azobenzene, the broad bands seen at ordinary temperatures are broken into a series of narrow but still diffuse bands at −196°C., forming a line spectrum at 20°Abs.

Aside from the obliteration of the finer structure, the situation of the absorption region may be either unaffected or shifted to other wave-lengths by the presence of a solvent. Instances in which there is similarity in absorption in the gas phase and in liquid solution are found in the halogens as vapors or in solution in carbon tetrachloride, chloroform or carbon disulfide, and for hydrogen sulfide in water and in hexane. When the solute is solvated, there may, however, be marked shifts in the situation and intensity of the absorption bands.[9] The effects of variation of temperature on the extinction coefficients of a number of salt solutions, mostly colored, have been measured by Mukerji, Bhattacharji and Dhar.[10] The changes are in large part attributed to changes in the hydration of the solutes, usually ions, at higher temperatures.

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[4] Dickinson, R. G., *Chem. Rev.*, **17**, 413 (1935); *J. Phys. Chem.*, **42**, 739 (1938); see also Rollefson, G. K., and Libby, W. F, *J. Chem. Physics*, **5**, 569 (1937).

[5] West, W., and Ginsburg, E., *J. Am. Chem. Soc.*, **56**, 2626 (1934).

[6] For further discussion of the modifications of the quantum yield of the primary process which may occur in solution, see also Kistiakowsky, G. B., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 44 (1935), and Rabinowitsch, E., and Wood, W., *Trans. Faraday Soc.*, **32**, 1381 (1936).

[7] Rollefson, G. K., *Chem. Rev.*, **17**, 425 (1935); *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 19 (1935); *Chem. Abs.*, **30**, 6648 (1936).

[8] Obreimow, I., and de Haas, W. J., *Proc. K. Acad. Wetensch. Amsterdam*, **31**, 353 (1928); Schaumann, H., *Z. Physik*, **76**, 106 (1932).

There have been many studies of the absorption spectra of salts in solution, the absorption of the solution being due in large part to absorption by the ions present. The influence of electrostatic forces upon the magnitudes of the extinction coefficients in various solutions and the effects of adding foreign non-absorbing salts have been investigated, but for present purposes it is sufficient to note that the effects of these electrostatic forces may be great enough to alter markedly the absorption region from that of the pure undissociated compound. The result may be that in solutions the photochemically effective wave-length regions may differ from those which induce the same reaction in the gas phase.[11] For example, the absorption band of the iodide ion found at 2273A in aqueous solution shifts toward shorter wave-lengths in concentrated calcium chloride solutions and in alcohol. Changes in the solvation of the ions are of importance in producing these effects.[12] Scheibe [13] has reviewed the causes of variations in the absorption spectra of solutions.

Cations of the alkalies and alkaline earths do not absorb light, and visible or ultraviolet absorption exhibited by solutions of their salts is usually due to the anions. Other cations, as those of the transitional group of elements, iron, chromium, copper, cobalt, nickel, or manganese, exhibit absorption believed to arise from low-energy electron shifts involving the incomplete electron shell in the structure of these atoms.[14]

Electron-Affinity Spectra. The spectra of the anions, particularly those of the halogens, have been called "electron affinity spectra," since it is considered that the electron held by the atom or radical as ion is driven off from it in the absorption process, rather than excited to a higher energy state.[15] The iodide ion exhibits two broad continuous bands with maxima at about 2250 and 1950A (see Figure 113). The separation between these maxima when expressed as the difference in the corresponding wave-numbers (about 8000 cm^{-1}.) is very close to the difference between the ground state and an excitation state of the iodine atom (7600 cm^{-1}.). Thus one maximum is interpreted as caused by separation of an electron from a normal iodine ion and the other to separation of an electron from an excited ion. The hydration of the ion and the hydration of the electron modify the results somewhat. Franck and Haber [16] have postulated that, as a part of the process, the electron attaches itself to an OH group split off from a molecule of hydration of the ion, a hydrogen atom being also formed. Similar considerations also apply to the spectra of other anions, but in the more complex ones, as the nitrate ion, other decomposition possibilities must also be considered. Farkas and Farkas modify the theory by assuming that the primary process involves a transfer of the electron from the anion to a water molecule in the hydration layers. If no photochemical change ensues, the electron returns to the initial state. If a reaction occurs, the final state is reached by the transfer of the electron to a positive ion. Thus,

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[9] Hantzsch, A., and Carlsohn, H., *Z. anorg. Chem.*, **156,** 199 (1926).

[10] Mukerji, B. K., Bhattacharji, A. K., and Dhar, N. R., *J. Phys. Chem.*, **32,** 1834 (1928).

[11] von Halban, H., and Ebert, L., *Z. physik. Chem.*, **112,** 321 (1924); von Halban, H., *Trans. Faraday Soc.*, **21,** 620 (1926); von Halban, H., and Eisenbrand, J., *Z. physik. Chem.*, **122,** 337 (1926).

[12] Scheibe, G., with Römer, R., and Rössler, G., *Ber.*, **59B,** 1321, 2616 (1926).

[13] Scheibe, G., *Angew. Chem.*, **50,** 212 (1937).

[14] Saha, M., *Nature,* **125,** 130 (1930); Shibata, Y., and Harai, K., *J. Chem. Soc. Japan,* **56,** 1 (1935); Pestemer, M., and Bernstein, P., *Z. anorg. allgem. Chem.*, **223,** 121 (1935); Samuel, R., and others, *Z. physik. Chem.*, **22B,** 431 (1933); *Bull Acad. Sci. United Provinces Agra Oudh, Allahabad,* **3,** 157 (1934); *Trans. Faraday Soc.*, **31,** 423 (1935); *Indian J. Physics,* **9,** 491 (1935); Inoue, T., *J. Chem. Soc. Japan,* **54,** 65 (1933); *Chem. Abs.*, **27,** 2382 (1933).

$$(I^-.H_2O) + h\nu \longrightarrow I.H_2O^-$$
$$I.H_2O^- + (H^+) \longrightarrow I + H_2O + H.$$

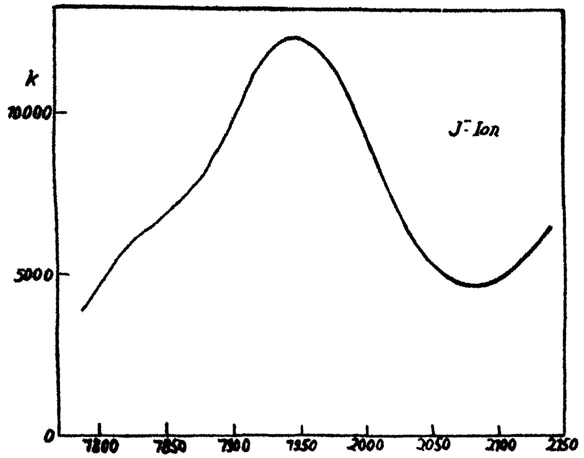

FIGURE 113. Electron Affinity Spectrum for Iodide Ion (Franck and Scheibe, *Z. physikalische Chemie*).

Lederle[17] concludes, as a result of measurements of the electron-affinity spectra of aqueous and alcoholic solutions of alkali and alkaline earth halides, that the effects of temperature and solvent may be satisfactorily explained by the hypothesis of Franck and Scheibe. The hydroxyl ion has an absorption maximum at 1860A.[18]

Since the theory of photochemical reactions in liquid systems is less advanced than is that of reactions in gaseous systems, the treatment of much of the material in this chapter is necessarily of a more descriptive and qualitative nature than that of the preceding chapter. On the other hand, photochemical processes in crystals, particularly the alkali and silver halides, are now being very actively studied from a theoretical standpoint.

WATER AND HYDROGEN PEROXIDE

Water is very transparent to ultraviolet wave-lengths greater than 1950A, but below this its transparency decreases rapidly.[19] Although earlier observers[20] had

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[15] Franck, J., and Scheibe, G., *Z. physik. Chem.*, **4B**, 22 (1928); **5B**, 355 (1929); Fromherz, H., and Menschick, W., *Z. physik. Chem.*, **7B**, 439 (1930); Farkas, A., and Farkas, L., *Trans Faraday Soc.*, **34**, 1113 (1938).

[16] Franck, J., and Haber, F., *Ber. Berl. Akad.*, 250 (1931); Scheibe, G., *Z. Elektrochem.*, **35**, 701 (1929); *Sitzb. phys.-med. Soc. Erlangen*, 58-59 (1927); *Chem. Abs.*, **22**, 4371 (1928). See also Dutta, A. K., *Trans. Bose Research Inst., Calcutta*, **10**, 209 (1934-5), *Chem. Abs.*, **32**, 3263 (1938); Farkas, A., and Farkas, L., *Trans. Faraday Soc.*, **34**, 1113, 1120 (1938).

[17] Lederle, E., *Z. physik. Chem.*, **10B**, 121 (1930).

[18] Ley, H., and Arends, B., *Z. physik. Chem.*, **6B**, 240 (1929).

[19] Tsukamoto, K., *Rev. d'optique*, **7**, 89 (1928); for data throughout the visible see Hulburt, E. O., and Dawson, L. H., *J. Opt. Soc. Am.*, **24**, 175 (1934) and for sea water, Hulburt, E. O., *Ibid*, **17**, 15 (1928).

[20] Kernbaum, M., *Farm. Polsk.*, **16**, 71 (1913); *Chem. Abs.*, **8**, 387 (1914).

concluded that ultraviolet rays, and even the rays of the sun, would cause some decomposition of pure oxygen-free water, with the production of hydrogen peroxide, subsequent work has shown that only radiations of very short wave-length[21] (1900A) produce any effect. Tian states that if the water contains dissolved oxygen, this may react with the hydrogen set free in the primary decomposition to form hydrogen peroxide. Ozone, formed from oxygen, may further react with hydrogen peroxide.[22] Further work is needed.

It has been found by Bowden[23] that if, during the electrolysis of dilute sulfuric acid, the mercury cathode is irradiated by wave-lengths less than 4000A, there is a marked acceleration of the deposition of hydrogen. A similar effect occurs with respect to the liberation of oxygen at a platinum electrode, but the threshold wave-length was not determined.[24]

The sensitized formation of hydrogen peroxide in the presence of aqueous suspensions of zinc oxide (in contact with air) when exposed to sunlight has been described by Baur and Neuweiler,[25] who represent the process in terms of the "molecular electrolysis" theory of photosensitization discussed in Chapter 16. The yield was said to be greatly increased in the presence of small amounts of glycerol, dextrose or benzidine, these added substances being simultaneously oxidized. When glycerol was employed, there was an indication of the formation of dihydroxyacetone and possibly glycerose; with benzidine, a brown, insoluble oxidation product resulted. When the sensitizer was eosin or fluorescein rather than zinc oxide, the formation of hydrogen peroxide could be observed only when dextrose or benzidine, but not glycerol, was present.

The Decomposition of Hydrogen Peroxide. In solutions, the coefficients of absorption of hydrogen peroxide are the same as those for the vapor.[26] The absorption, which begins between 3700 and 3800A, is but slight to 3000A, after which it increases rapidly with decreasing wave-length. In Figure 112, the circles represent values for the solutions and the crosses those for the vapor. Sharma[27] concludes the abrupt termination of the absorption spectra of 3, 10 and 30 per cent solutions at 2055A to correspond to the dissociation $H_2O_2 + h\nu \rightarrow 2H + O_2$.[28] The progressive addition of alkali displaces the absorption curves toward longer wave-lengths, a limiting value of the shift (500A) being attained when the ratio of alkali to peroxide is one to one. The new absorption is attributed to the ion HO_2', the formation of which involves a change in the mode of interatomic linking.[29]

It was early found that the velocity of decomposition of hydrogen peroxide in dilute aqueous solution increases with increasing frequency of the radiation employed.[30] It has been observed that with dilute solutions of the peroxide, the velocity is dependent on the concentration.[31] Tian and also Henri and Wurmser believed the velocity of decomposition to be proportional to the intensity of the incident radiation rather than to that absorbed. Qureshi and Rahman[32] state however, that the rate is proportional to the square root of the light intensity In recent observations, Kornfeld[33] concluded that in neutral solutions, the rate of decomposition produced by the 3110A line is proportional to the product of the concentration of hydrogen peroxide and the square root of the absorbed light This relationship fails in acid solutions. This may have been a contributing factor in causing the divergent results of previous observers. Also Kornfeld noted that the quantum yield is variable and large, sometimes being as high as 80.

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[21] Tian, A., *Compt. rend*, **156**, 1063 (1913); Houben, J., and Fischer, W., *Arb. biol. Reichs. Land-Forstw.*, **15**, 601 (1928); *Chem. Abs.*, **23**, 2366 (1929); Coehn, A., *Ber.*, **43**, 880 (1910).

[22] See also Kernbaum, M., *Compt. rend.*, **149**, 273 (1929).

[23] Bowden, F. P., *Trans. Faraday Soc.*, **27**, 505 (1931).

[24] See also Audubert, R., *Compt. rend.*, **189**, 1265 (1929).

[25] Baur, E., and Neuweiler, C., *Helv. Chim. Acta*, **10**, 901 (1927).

[26] Urey, H. C., Dawsey, L. H., and Rice, F. O., *J. Am. Chem. Soc.*, **51**, 1371 (1929).

[27] Sharma, R. S., *Proc. Acad. Sci. United Provinces Agra Oudh, India*, **4**, 51 (1934); *Chem. Abs.*, **29**, 7187 (1935).

[28] For a comparison with the absorption of mono- and di-alkyl peroxides, see Lederle, E., and Rieche, A., *Ber.*, **62B**, 2573 (1929).

[29] Bredig, G., Lehmann, H. L., and Kuhn, W., *Z. anorg. Chem.*, **218**, 16 (1934).

[30] Tian, A., *J. Chem. Soc.*, **108** (ii), 828 (1915); *J. Soc. Chem. Ind.*, **35**, 114 (1916); *Chem. Abs.*, **10**, 1960 (1916).

[31] Tian, A., *l. c.*; Kornfeld, G., *Z. wiss. Phot.*, **21**, 66 (1921); Henri, V., and Wurmser, R., *Compt. rend.*, **157**, 1261 (1913); **156**, 1012 (1913).

The presence of dust in the water used as solvent has been found to affect the results,[34] the rate of decomposition being roughly proportional to the dust content. Qureshi and Rahman found the quantum yield to vary with decreasing concentration between about seven and three, there being a maximum of eleven at a concentration of 0.09 M. Kornfeld proposed a chain mechanism for the reaction applicable in the presence of sodium sulfate and sulfuric acid:

$$\begin{aligned} H_2O_2 + h\nu &\longrightarrow 2OH \\ H_2O_2 + OH &\longrightarrow H_2O + HO_2 \\ H_2O_2 + O_2 &\longrightarrow O_2 + OH + OH \\ OH + O_2H &\longrightarrow H_2O + O_2. \end{aligned}$$

In neutral solutions longer chains might account for the higher yields. Heidt,[35] using light of high intensity at 3130A, found the quantum yield to approach unity as the concentration of the hydrogen peroxide was decreased to low values. As is usually the case with chain reactions, the decomposition is readily inhibited by traces of various substances. Henri and Wurmser observed this stabilizing action on hydrogen peroxide as early as 1913. Anderson and Taylor[36] noted that although many inhibitors might function by absorbing the effective rays, some of the most effective inhibitors did not absorb the destructive wave-lengths. Furthermore, the inhibitors in general acted much more effectively when placed within the solution than when employed as external light filters. Subsequent work on the susceptibility of chain processes to inhibitors has given a new conception of the action of the latter as efficient breakers of chains. This topic is discussed in somewhat greater detail in connection with the oxidation of sulfites, but for a more general treatment, the reader is referred to texts on the theory of chain reactions.[37]

Among the most efficient inhibitors for decomposition of hydrogen peroxide found by Anderson and Taylor were ethylamine, aniline, phenol and quinine salts. Strong to fairly strong inhibitors included methyl benzoate, benzamide and acetanilide. Moderate inhibitors were hydrocinnamic acid, ethyl cinnamate methyl oxalate, ethyl alcohol and benzyl alcohol. Weak inhibitors included ethyl benzoate, ethyl phenylacetate, acetone, acetophenone, benzophenone and benzene Acetic acid, ethyl acetate and acetamide had little or no effect. In most cases the concentrations of inhibitor employed ranged from 0.0001 to 0.005 per cent. Anderson and Taylor[38] concluded that inorganic bases are excellent inhibitors, inorganic acids are good inhibitors, bromides and chlorides have a moderate inhibitory action and other inorganic salts such as nitrites, sulfates and perchlorates, have no action. They found also that one hydroxyl ion inhibits as much as 25 hydrogen ions and that inhibition has a zero temperature coefficient.

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[32] Qureshi, M., and Rahman, M. K., *J. Phys Chem.*, **36**, 664 (1932).

[33] Kornfeld, G., *Z. physik Chem.*, **29B**, 205 (1935).

[34] Rice, F. O., and Kilpatrick, M. L., *J. Phys. Chem.*, **31**, 1507 (1927)

[35] Heidt, L. J., *J. Am. Chem. Soc.*, **54**, 2840 (1932).

[36] Anderson, W. T., Jr., and Taylor, H. S., *J. Am. Chem. Soc.*, **45**, 650 (1923).

[37] Semenoff, N., "Chemical Kinetics and Chain Reactions," Oxford University Press, 1935.

[38] Anderson, W. T., Jr., and Taylor, H. S., *J. Am. Chem. Soc.*, **45**, 1210 (1923); see also Mathews J. H., and Curtis, H. A., *J. Phys. Chem.*, **18**, 521 (1914).

Recently, Dain and Shvartz[39] concluded that the photochemical decomposition is defined by the rate equation:

$$-d(H_2O_2)/dt = kI^{1/2}(H_2O_2)^{1/2}.$$

At 75° and under irradiation by a mercury vapor lamp, the rate of decomposition is reduced to one-half by the addition of 91×10^{-4} mole per liter of dimethyl ketone, of 20×10^{-4} of methyl ethyl ketone, or of 26×10^{-4} of diethyl ketone. The correction for the internal absorption of light by the ketone was never over 5 per cent. The ratios of the velocities of the inhibited and uninhibited reactions are linear functions of the ketone concentration. They believe the ketones decrease the initial number of chains, rather than break those already formed.

The well-known catalytic activity of lead peroxide and of platinum in the thermal decomposition of hydrogen peroxide is said to be increased by previously exposing the catalysts to ultraviolet light.[40] Irradiation during thermal decomposition increases the activity of graphite, charcoal and lead peroxide as catalysts, but may decrease that of platinum. It is suggested that electrons are transferred from hydrogen peroxide molecules adsorbed on inactive regions of the catalyst to those on active centers.

Sensitization of the decomposition of hydrogen peroxide to visible light has long been known. Kistiakowsky,[41] who used as sensitizer a mixture of potassium ferro- and ferricyanides, found the decomposition to follow a monomolecular course and to continue after the irradiation had ceased. According to Weigert,[42] potassium ferrocyanide which has been irradiated will cause a reaction when added to hydrogen peroxide in the dark. The same phenomenon has been found also in the case of sodium nitroprusside by Qureshi,[43] who believes the irradiation of this compound produces some colloidal Prussian blue which may serve as a catalyst for the dark reaction.

The quantum yield for the bromine-sensitized reaction has been found by Livingston and Schoeld[44] to be less than unity, but Griffith and McKeown[45] find the yield much greater than one in blue light. They also deny the existence of a "photo-stationary" state in this system.

Notwithstanding the fact that the decomposition of hydrogen peroxide is so sensitive to dust, inhibitors and sensitizers, the reaction has been employed in actinometry by Koeppe.[46] However, Sostmann[47] found this method of measuring radiations unreliable.

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[39] Dain, B. Y., and Shvartz, A. S., *Acta Physicochim. U.R S.S.*, **3**, 291 (1935); *J. Phys. Chem. (U.S.S.R.)*, **7**, No. 2 (1936); *Chem. Abs.*, **30**, 2109 (1936).

[40] Pisarshevskii, L. V., Korabel'nik, R. K., and Rinskaja, E. S., *Bull. Acad. Sci. U.R.S.S.*, **7**, 931 (1934); *Brit. Chem. Abs.* **A**, 47 (1935); *Chem. Abs.*, **29**, 2433 (1935).

[41] Kistiakowsky, G. B., *Z. physik. Chem.*, **35**, 431 (1901).

[42] Weigert, F., *Ann. Physik*, **24**, 261 (1907).

[43] Qureshi, M., *J. Phys. Chem*, **35**, 656 (1931).

[44] Livingston, R., and Schoeld, E. A., *J. Am. Chem. Soc.*, **58**, 1244 (1936).

[45] Griffith, R. O, and McKeown, A., *J. Am. Chem. Soc.*, **58**, 2556 (1936).

[46] Koeppe, H., *Arch. Kinderheilk.*, **89**, 26 (1929-30).

[47] Sostmann, H., *Strahlentherapie*, **51**, 359 (1934); *Chem. Abs*, **29**, 1012 (1935).

Photochemistry of the Halogens and Alkali Halides

The decomposition of 0.08 to 1.16 molar solutions of hydrogen iodide in hexane by a spark follows Einstein's law.[48] At the higher concentration, the quantum yield was, as in the gas phase, two. At lower concentrations, it dropped to one because the hydrogen and iodine atoms liberated by absorption may recombine as a result of collisions with the solvent molecules which carry off the excess energy. But in aqueous solutions, the specific photochemical yield, that is, the number of molecules decomposed per gram calorie absorbed, decreased with the use of increasing wave-lengths. This is contrary to the Einstein law, since at longer wave-lengths a constant amount of energy is divided between a greater number of smaller quanta and should, therefore, bring more molecules into reaction. Furthermore, the yields decreased rapidly as the concentrations of the aqueous solutions were decreased. In highly concentrated aqueous solutions (7.5 normal) the shortest wave-length used (2070A) gave an apparent quantum yield greater than two. To explain this it was suggested that an activated hydrogen iodide molecule might react with several consecutive normal molecules. Warburg believed also that the iodide ion forms no free iodine when irradiated, any production of iodine resulting from a decomposition of hydrogen iodide molecules. This explanation is not in line with the theory of complete dissociation of strong electrolytes. The anomalous effect of the wave-lengths was assumed due to the existence of hydrates of hydrogen iodide, since in hexane solutions the behavior was normal with respect to wave-length.

Subsequent to the development of the Franck and Haber theory of the primary process of absorption by halogen ions, $I^-(H_2O)+h\nu \rightarrow I+H+OH^-$ it became evident that the low yields in dilute solution may be explained as due to a combination of the hydrogen and iodine atoms which result from this process. The resulting hydrogen iodide then dissociates into hydrogen ions and iodide ions, the former combining with the hydroxyl ion formed in the primary process to yield water. In this way the original system present before the absorption of light is restored. In higher concentrations, the mechanism of the primary process, contrary to the assumption of Warburg, remains the same. In this case, however, there are present so many $I^-(H_2O)$ ions that the hydrogen atoms produced in the primary process may collide with the hydrated ions (rather than with iodine atoms) to produce a second iodine atom, an hydroxyl ion and a hydrogen molecule. The two iodine atoms may then combine to form a molecule of iodine. In this way, the quantum yields increase with the concentration to a value of about two as in the gas phase reaction.[49]

Butkov[50] studied the effect of various wave-lengths upon half-normal solutions of caesium, potassium and sodium iodides, and also upon more dilute solutions of the latter salt (*N*/50). He found that spark lines longer than 2700A failed to cause liberation of free iodine, this wave-length agreeing with the beginning of the absorption band of the iodide ion. Various shorter wave-length lines, notably the 2573A line, were effective in liberating iodine. In accordance with the Franck-Haber mechanism, the solutions in which iodine was liberated became more alkaline. The quantum yields in these experiments were, however, lower than those of Warburg and Rump in stronger hydrogen iodide solutions. Butkov placed the limit for the reaction in bromides, in which the yields of free bromine were lower, between 2265 and 2313A. He was unable to detect the liberation of chlorine from chlorides, the absorption of the chloride ion being located at wave-lengths shorter than 1900A.[51]

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[48] Warburg, E., and Rump, W., *Z. Physik*, **47**, 305 (1928).

[49] Compare Farkas, A., and Farkas, L., *Trans. Faraday Soc.*, **34**, 1120 (1938). They were particularly concerned with the separation of hydrogen isotopes, when heavy water was in the solvent.

[50] Butkov, K., *Z. Physik*, **62**, 71 (1930).

Oxidation of Iodides. Earlier observations of the liberation of iodine from solutions of potassium iodide were in most cases complicated by photo-öxidations, since oxygen was rarely excluded from the solutions.[52] The influence of oxygen upon the photochemistry of potassium iodide has been shown quantitatively by Krauss and Bruchhaus.[53] An oxygen-containing solution on irradiation gave 4.92 per cent decomposition, but a similar solution previously boiled to remove the air, gave only a 0.76 per cent separation of iodine.

In testing the ability of variously colored glass bottles to protect drugs from the action of light, Jermstad and Østby[54] employed a 2-per cent potassium iodide solution to which had been added 4 per cent of dilute sulfuric acid. This was exposed in the bottles to be tested for one-half hour to a quartz lamp or for one hour to sunlight. A maximum separation of 1.5 mg. of iodine after this time was considered permissible. Black, red and all-brown glasses were satisfactory, although the latter gave 1.10 mg. of iodine in ultraviolet light or 0.50 mg. in sunlight. It is difficult to understand which components of the solution can absorb the wave-lengths available in such experiments, unless it might be the tri-iodide ion. It has been stated that even in darkness, hydrogen ions can catalyze oxidation to some extent.

Stobbe and Steinberger[55] found irradiation of alkaline solutions of potassium iodide in quartz or Uviol vessels to sunlight or the quartz mercury arc to cause a diminution of the alkalinity, probably because of the absorption of carbon dioxide from the air. If the solutions were originally but slightly alkaline, irradiation produced free iodine and hypoiodide. If the alkalinity was somewhat greater, iodate appeared also. In strongly alkaline solutions, the iodate was the only product. In neutral solutions there was but little reaction, but the addition of increasing amounts of carbon dioxide increased the photolysis through a maximum. The oxidation of neutral iodide solutions is a bimolecular reaction. The velocity coefficient is dependent on the wave-length and intensity of the light absorbed. It increases with time until so much tri-iodide ion has formed that the absorption of all available radiation is complete.

According to Berthoud and Nicolet,[56] the oxidation of hydriodic acid by oxygen in red light has a velocity which can be expressed by

$$\frac{d\,[I_3]}{dt} = k(KI)^{n}(O_2)\sqrt{I_0(I_3^-)\,(H_2SO_4)}$$

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[51] Extensive data on the absorption of liquid hydrogen chloride and concentrated hydrochloric acid solutions have been given by Tréhin, R., *Compt rend.*, **191**, 774 (1930); **193**, 1089 (1931); **195**, 1269 (1932), **199**, 1047 (1934); **200**, 1663 (1935); *J. Phys. Radium*, **4**, 449 (1933). Data for a number of chlorides are included and indicate that in concentrated solutions these are not as transparent to the region 2170 to 2500A as had been assumed from measurements on more dilute solutions. See also Huttig, G., and Kukenthal, H., *Z. Elektrochem.*, **34**, 14 (1928) and Hantzsch, A., *Ber.*, **59B**, 1096 (1926). For earlier data, Getman, F. H., *J. Phys. Chem.*, **29**, 853 (1925), and Brannigan, P. J, and Macbeth, A. K., *Chem. Abs*, **11**, 313 (1917). In the presence of free halogen, the absorption is altered because of the formation of trihalogen ions. Similar behavior is also encountered in alcoholic solutions, according to Job, P., *Compt rend.*, **182**, 632, 1631 (1926).

[52] Suryanarayana, K., *J. Sci. Assoc. Maharajah's College, Vizianagaram*, **2**, 12 (1924); *Chem. Abs*, **18**, 3548 (1924); Ross, W., *J. Am. Chem. Soc.*, **28**, 788 (1906); Kailan, A., *Monatsh.*, **34**, 1225 (1913); *Chem. Abs.*, **8**, 14 (1914).

[53] Krauss, F., and Bruchhaus, E, *Z. anorg. allgem Chem.*, **189**, 53 (1930); *Brit Chem. Abs.*, **A**, 553 (1930); earlier experiments were due to Plotnikow, J., *Z. physik. Chem*, **58**, 214 (1907).

[54] Jermstad, A., and Østby, O., *Arch. Pharm. Chem.*, **92**, 463 (1935); *Chem. Abs.*, **29**, 7599 (1935).

[55] Stobbe, H., and Steinberger, F. K., *Z. anorg. Chem.*, **161**, 21 (1927).

In blue light, the velocity also increases as the square root of the light intensity. The photochemical reaction has a very small temperature coefficient, which Vita[57] believes depends in some manner upon the wave-length.[58] The influence of the presence of potassium dichromate and eosin in causing the separation of iodine from potassium iodide when illuminated has been studied by Reychler.[59]

The conductance of solutions of sodium iodide or of lithium bromide in acetophenone, but not of the solvent itself, decreases to a constant value when the solutions are exposed to light, and is restored to its former value when the solutions are returned to darkness.[60] A yellow color also appeared during irradiation. These results were confirmed by Morgan, Lammert and Crist,[61] who found also that solutions which had reached a constant conductance in glass would show a further decrease when placed in quartz vessels. The acetophenone is also decomposed with the formation of some benzoic acid. The quantity of iodine liberated from sodium iodide under these conditions was independent of the concentration of the salt, but depended upon the intensity of the radiation and the time of exposure, that is, upon the amount of acetophenone which had been decomposed.

The oxidation of ferrous ions by iodine, $2Fe^{++} + I_3 \rightarrow 2Fe^{+++} + 3I'$, was found to be photosensitive[62] in both the ultraviolet and the visible region of 5500 to 6500A (maximum at 5800A). Iodine, being present as the tri-iodide ion, was the photosensitive component of the solution, the iron salts or the iodide ion being practically inactive in the spectral regions employed. The temperature coefficient of the reaction is 1.17. From that of the dark reaction (2.71), it appeared that the energy of activation, 2.14 volts, was very close to a resonance potential of the iodine molecule (2.34 v.). For the wave-length 5790A, the quantum yield was found to be unity, one molecule of iodine reacting per absorbed quantum. Kistiakowsky[63] found this quantum yield given also by the wave-lengths 5460A, 4360 and 3660A, regions which Rideal and Williams had found ineffective. This absence of a maximum sensitivity at 5800A lessens the significance of the relation between the energy of activation and a critical potential of iodine noted by Rideal and Williams. By working with very dilute solutions at 0°C., and using light of wave-lengths greater than 5000A which had been freed from infrared rays, Ravitz and Dickinson[64] were able to show that, in the first stages of irradiation, light caused a reduction of the ferric ion by the iodide ion.

Mukerji and Dhar[65] found the reactions between iodine and such compounds as potassium formate, oxalate, ferrous sulfate and sodium nitrite to be accelerated principally by light in the range 3160 to 4600A. The quantum yields, calculated for 3880A, were low in the case of potassium oxalate, ferrous sulfate and sodium nitrite since for the transformation of each molecule of iodine there were required

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[56] Berthoud, A., and Nicolet, G., *Helv Chim. Acta*, **10**, 475 (1927); van Strachow, N., *Z. wiss. Phot.*, **18**, 267 (1919); *Chem. Centrbl.*, **90** (III), 309 (1919)

[57] Vita, N., *Gazz. Chim. Ital.*, **63**, 211 (1933).

[58] For comparisons of the kinetics of the photoxidation of the iodides of hydrogen and deuterium, see Cook, G. A., and Bates, J. R., *J. Am. Chem. Soc.*, **57**, 1775 (1935).

[59] Reychler, A., *Bull. Soc. Chim. Belg.*, **34**, 236 (1925); *Chem. Abs.*, **20**, 545 (1926). See also Winther, C., *Z. physik. Chem.*, **A174**, 41 (1935) and Tappeiner, H., *Chem. Centr.*, I, 1793 (1906); *Arch. klin. Med.*, **86**, 478.

[60] Dutoit, *Z. Elektrochem.*, **12**, 642 (1906); Nicollier, *Thesis*, Lausanne, 1907.

[61] Morgan, J. L. R., Lammert, O. M., and Crist, R. H., *J. Am. Chem. Soc.*, **46**, 1170 (1924).

[62] Rideal, E. K., and Williams, E. G., *J. Chem. Soc.*, **127**, 258 (1925); for previous observations, Sasaki, N., *Z. anorg. Chem.*, **122**, 61 (1922).

[63] Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **49**, 976 (1927).

[64] Ravitz, S. F., and Dickinson, R. G., *J. Am. Chem. Soc.*, **53**, 3381 (1931).

[65] Mukerji, B. K., and Dhar, N. R., *Z. Elektrochem.*, **31**, 621 (1925); Bhattacharya, A. K., and Dhar, N. R., *Z. anorg. allgem. Chem.*, **196**, 26 (1931).

28, 15 and 49 quanta, respectively. In later work, Bhattacharya and Dhar[66] stated that the quantum yield in the reaction with sodium nitrite varies greatly at different temperatures and with different wave-lengths. The dark reaction is bimolecular and has a temperature coefficient of 2.7, that of the light reaction varying from 2.07 at 4725A to 2.35 at 8500A.

According to Batley,[67] the maxima observed in the absorption of alcoholic solutions of iodine at 3600 and 2900A are due to the formation of HI_3. When isolated in the solid form on gelatin, this has a maximum at 3680A. The true iodine curve, determined in the presence of ozone which decomposed the hydrogen iodides, shows only one maximum at 4770A and general absorption in the far ultraviolet. Formation of the hydrogen iodides is attributed to a slow photochemical reaction $C_2H_5OH + I_2 \rightarrow CH_3CHO + 2HI$, followed by an instantaneous reaction $I_2 + HI \rightarrow HI_3$.

Terenin[68] has studied the photochemical changes which occur in a layer of iodine molecules adsorbed on thallium iodide. Light, particularly of wave-length 5600A, produces a discoloration attributed to photodissociation of adsorbed molecules. The liberated iodine atoms are then bound by thallium ions. The presence of adsorbed hydrogen or oxygen molecules on the surface causes marked shifts of the wave-lengths which are active, but nitrogen has no effect. The results are ascribed to photochemical reactions between adsorbed iodine and hydrogen or oxygen, with the formation of hydrogen iodide and of iodine oxide.

Potassium iodate, when irradiated by short wave-lengths in a solution saturated with carbon dioxide, liberates iodine at a rate which is linear so long as the amount liberated is small compared with the total amount present as iodate.[69] In the presence of air, the rate of the reaction decreases slowly with time. When the solution is kept saturated with oxygen, iodine is not liberated. Carbon dioxide greatly increases the rate of photolysis.

Bromine. Bovis[70] finds bromine in water, carbon tetrachloride, chloroform or alcohol to show two absorption maxima of which one lies at 4100A and the other at 2600A. Since only the former is also exhibited by gaseous and by liquid bromine, the band at 2600A must be characteristic of bromine in solution.

Photochemical reaction between bromine and water appears to follow the reactions:[71]

$$Br_2 + H_2O \longrightarrow H^+ + Br' + HOBr$$
$$HOBr + h\nu \longrightarrow H^+ + Br' + 1/2O_2$$

The rate decreases with increasing bromide-ion concentration.

In light of wave-length 4360A, carbon tetrabromide is oxidized when present in concentrations above 0.05 mole per liter.

$$2CBr_4 + O_2 \longrightarrow 2COBr_2 + 2Br_2$$

At lower concentrations, the oxygen consumption is greater. The quantum yield is less than one. The reaction is accelerated by oxygen, retarded by bromine and unaffected by bromophosgene.[72] The suggested mechanism involves the primary removal of a bromine atom, which requires at most 50 kcal. The resulting CBr_3 then reacts with the oxygen.

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[66] Bhattacharya, A. K., and Dhar, N. R., *J. Indian Chem. Soc.*, **7**, 709 (1930); *Chem. Abs.*, **25**, 251 (1931).

[67] Batley, A., *Trans. Faraday Soc.*, **24**, 438 (1928); *cf.* also Rabinowitsch, E., and Wood, W. C., *Ibid.*, **32**, 547 (1936).

[68] Terenin, A., *Acta Physicochim, U.R.S.S.*, **1**, 178, 407 (1934); *Chem. Abs.*; **29**, 685, 7810 (1935). *Brit. Chem. Abs.*, **A**, 943 (1935).

[69] Mathews, J. H., and Curtis, H. A., *J. Phys. Chem.*, **18**, 641 (1914); *J. Chem Soc.*, **106** (ii), 830 (1914).

[70] Bovis, P., *Compt. rend*, **185**, 57 (1927).

[71] Pagel, H. A., and Carlson, W. W., *J. Phys. Chem.*, **40**, 613 (1936).

Bromine oxide, Br_2O, prepared by the interaction of mercury oxide and bromine in carbon tetrachloride solution, decomposes in light by the following two reactions: [73]

$$Br_2O \longrightarrow Br_2 + 1/2O_2$$
$$Br_2O + CCl_4 \longrightarrow COCl_2 + Br_2 + Cl_2.$$

The maximum rate of decomposition of bromine chloride in the light is four times that in the dark. The quantum yield is of the order of a thousand.[74]

Chlorine. That sunlight decomposes chlorine water with the formation of oxygen and chlorides, or under certain circumstances, of chlorites and chlorates, has long been known. The loss of active chlorine in bleaching solutions in daylight has been found to be after 70 days in filled white glass bottles, 48 to 61 per cent, in half-filled bottles, 63 to 76 per cent and in half-filled brown bottles, 11 to 29 per cent.[75]

Free hypochlorous acid is said to be less sensitive to light than the sodium salt.[76] Sunlight, diffused daylight and the lines at 3130, 3650 and 4360A, appeared equally effective.[77] Despite repeated and detailed investigations, the interpretation of the reaction is not yet entirely clear. Neither hydrogen peroxide nor perchloric acid is formed, the only reaction products being hydrochloric acid, oxygen and chloric acid. To determine whether chlorine, hypochlorous acid or its ion is the photosensitive substance, Allmand and co-workers studied the effects on the rate and products formed, of the addition of various salts which might shift the equilibrium in the irradiated solutions. From the retarding effects of chlorides [78] or hydrochloric acid and the accelerating effects of buffer salts, they concluded that hypochlorous acid plays a more important part in the primary process than chlorine. The latter could not, however, be excluded, so that it was necessary to conclude that there may be two independent primary processes and two reaction mechanisms. In one at least, atomic oxygen was regarded as a primary product which, reacting with hypochlorous acid, produced chloric acid. When chlorine water was irradiated with a filtered band of mean wave-length 3650A, the quantum yield was approximately two. This was greatly decreased by the addition of hydrochloric acid (to 0.054 in 0.6*N* HCl). They believed an analysis of their data permitted an estimation of the quantum yield of the primary process (as distinguished from that of the overall reaction) as approximately unity. The temperature coefficient of the overall reaction was given as 1.4 by Benrath and Tuchel.[79]

The decomposition of sodium hypochlorite in neutral or alkaline solutions by wave-lengths in the range 4360-2130A was found to follow a monomolecular course by Lewis.[80] Allmand and Webb[81] found the proportion of sodium chlorate formed (40 to 53 per cent) to be independent of the intensity of illumination, hypochlorite concentration (0.08 to 0.01 molar) and of the concentrations of chloride, sulfate and free alkali. At higher dilutions, the yield of chlorate diminished. However, the yield of the latter increased with frequency of the light. The quantum yield was about unity at 3650A, slightly higher, 1.2, at 3130A and much higher, 4.7, at 2540A. The addition of electrolytes had an effect opposite to that previously noted in the case of hypochlorous acid or chlorine water. Thus, sodium chloride increased the quantum yield.

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[72] Koblitz, W., Meissner, H., and Schumacher, H. J., *Ber.*, **70B**, 1080 (1937)

[73] Brenschede, W., and Schumacher, H. J., *Z. physik. Chem.*, **29B**, 356 (1935).

[74] Brauer, G., and Victor, E., *Z. Elektrochem.*, **41**, 508 (1935)

[75] Tuenter, J. P. A., *Chem. Weekblad*, **32**, 429 (1935); *Chem. Abs.*, **30**, 28 (1936); see also, Fowler, *J. Chem. Soc.*, **94**, (II), 914 (1908); Kling, A., and Schmutz, R., *Compt. rend.*, **192**, 1655 (1931) and Jacquemaine, R. P., and Doll, J. H., *Bull. Soc. Chim.*, **2**, 1669 (1935); *Brit. Chem. Abs.*, **A**, 1331 (1935).

[76] Bonnet, L., *Rev. gen. mat. color.*, **39**, 29 (1935); *Chem. Abs.*, **29**, 2312 (1935).

[77] Allmand, A. J., Cunliffe, P. W., and Maddison, R. E. W., *J. Chem. Soc.*, **127**, 655, 822 (1925).

[78] See, however, Shilov, E. A., and Kupinskaya, G. V., *Byull. IvNITI*, **12**, No. 6, 39 (1936); *Chem. Abs.*, **31**, 3288 (1937).

[79] Benrath, A., and Tuchel, H., *Z. wiss. Phot.*, **13**, 383 (1913).

Chlorine Monoxide. Bowen stated that light (4100-4700A) acting on chlorine monoxide in carbon tetrachloride solution[82] caused formation of chlorine and oxygen. The quantum efficiency was calculated to be 0.81 to 1.02, on the assumption that these were the only products formed. In later work, however, Bowen observed that in the gaseous state two molecules of chlorine monoxide were decomposed by each absorbed quantum.[83] In the decomposition of chlorine monoxide in solution chlorine dioxide appears in appreciable amounts in comparison with the amount of monoxide decomposed, according to Dickinson and Jeffreys.[84] Using a method devised to eliminate the effects of the chlorine dioxide formed, they found that in solutions 0.014 to 0.054 molal in chlorine monoxide, the initial yield of chlorine dioxide is about 0.35 molecule per quantum absorbed. The initial rate of the decomposition of the chlorine monoxide has a quantum yield of at least 1.8. In a given run, the amount of the dioxide formed increases less and less rapidly with the number of quanta absorbed as the exposure is prolonged. This is possibly because the dioxide acts itself as an internal filter and also because it is also subject to photochemical decomposition.

Chlorine Dioxide. The decomposition of chlorine dioxide in carbon tetrachloride solutions (0.0346 to 0.317 molar) by blue and violet light was believed by Bowen[85] to have a quantum efficeincy of unity. A repetition of this work by methods[86] which also took into account the rapid dark reaction,[87] changed this value to two when the 4150A line was employed. The initial concentrations were 10.4 to 33.3 millimoles of chlorine dioxide per liter. Filters were used to limit the light to 4100 to 4200A. The filters were 30 mm. of a solution of 5.5 per cent of cobaltous sulfate (7 H_2O) and 8 per cent of ammonium thiocyanate and 30 mm. of a solution containing 25 per cent of copper sulfate (5 H_2O) and 0.04 per cent of quinine sulfate.

Since this radiation falls in the banded region of the spectrum of gaseous chlorine dioxide, it was assumed that activated molecules are formed. These on collision with the solvent molecules suffer decomposition by one of the following schemes:

$$\begin{aligned} ClO_2 &\longrightarrow Cl + O_2 \\ ClO_2 &\longrightarrow ClO + O \\ ClO_2 &\longrightarrow Cl + O + O. \end{aligned}$$

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[80] Lewis, W. C. McC , *J. Chem. Soc.*, **101**, 2371 (1912); Spencer, L., *Ibid.*, **105**, 2565 (1914).

[81] Allmand, A. J., and Webb, W. W., *Z. physik. Chem* , **131**, 189 (1928).

[82] Bowen, E. J., *J. Chem. Soc.*, **123**, 1199 (1923).

[83] Bowen, E. J., *J. Chem. Soc* , **123**, 2330 (1923).

[84] Dickinson, R. G , and Jeffreys, C. E. P., *J. Am. Chem. Soc* , **52**, 4288 (1930). It had, indeed, been observed to form in the gas phase reaction by Kistiakowsky, G. B., and Bodenstein, M., [*Z. physik. Chem.*, **116**, 371 (1925)], who believed the amounts small enough not to interfere with quantum yield measurements.

[85] Bowen, E. J., *J. Chem. Soc.*, **123**, 1199 (1923).

[86] Nagai, Y., and Goodeve, C. F., *Trans. Faraday Soc.*, **27**, 508 (1931).

[87] Luther, R., and Hoffmann, R., *Z. physik. Chem. Bodenstein-Festband*, 755 (**1931**).

It was believed that both of the two latter modes of decomposition required greater amounts of energy (80-85 kcal. for the second and 119 kcal. for the third) than is available at 4150A (69 kcal.). The first reaction is endothermic to the extent of only 2 kcal. For this reason the proposed mechanism which accounts for the yield of two, is

$$ClO_2 + h\nu \longrightarrow ClO_2^*$$
$$ClO_2^* \ (+ \ CCl_4) \longrightarrow Cl + O_2 \ (+CCl_4) + 67 \text{ kcal.}$$
$$Cl + ClO_2 \longrightarrow Cl_2O_2 + 56 \text{ kcal.}$$

Bowen and Cheung[88] found the quantum yield to increase from one at 4360A to two at 4050A or shorter wave-lengths. In aqueous solutions, the rate of photodecomposition was found proportional to the light intensity and the quantum yields were lower, being 0.2 at 4360A and unity at 3000A. Chlorine, chloride ion, and chlorate ions were identified. It was suggested that in solution, chlorine dioxide undergoes predissociation at lower energy values than it does as a gas.

In stable solutions prepared by washing the chlorine dioxide solutions with weakly alkaline materials, Luther and Hoffmann[89] found, after a pre-exposure to light, a decomposition to occur in the dark at a rate proportional to the four-thirds power of the concentration of chlorine dioxide. They suggested that chlorine monoxide liberated during the exposure to light may have induced the dark reaction. They also observed that the photolysis in ultraviolet light is a reaction of zero order. Spinks and Taube[90] find relatively large amounts of chlorine hexoxide, chlorine heptoxide and chlorine monoxide to be formed in addition to chlorine and oxygen. For a bromine-sensitized decomposition by the line 5460A, the quantum yield is 0.2 to 0.3.

Chlorates. Oertel[91] found that under the action of ultraviolet rays the alkali salts of chlorates, bromates, iodates and periodates in aqueous solution decompose into oxygen and halogen quantitatively if the exposure is sufficiently prolonged. Only a very small decomposition could be observed in the case of perchlorates. The rate of decomposition of bromates was greater than that of iodates and that of iodates greater than that of chlorates. Suryanarayana[92] states that neutral potassium chlorate and potassium nitrate solutions liberate oxygen on exposure to ultraviolet, but that equilibrium is quickly established. Exposure of a mixture of potassium chlorate and iodide with exclusion of oxygen leads to the oxidation of the iodide.

Solid potassium chlorate evolves oxygen when irradiated by radiations of wavelengths shorter than about 2800A.[93] The decomposition may also be brought about by the impact of 22-volt electrons, but those of lower voltages corresponding with 2800A could not be shown to be effective. According to Krishnan and Narayanaswamy,[94] photodissociation of the crystals shows an anisotropic effect, linearly polarized light producing a greater effect when the electric vector is in the plane of the chlorate ion than when it is along the normal to this plane.

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[88] Bowen, E. J., and Cheung, W. M., *J. Chem Soc.*, 1200 (**1932**).

[89] Luther, R., and Hoffmann, R., *Z. physik. Chem.*, **117A**, 17 (1936).

[90] Spinks, J. W. T., and Taube, H., *J. Am. Chem. Soc.*, **59**, 1155 (1937); *Can. J. Research*, **15B**, 499 (1937); *Chem. Abs.*, **32**, 2028 (1938).

[91] Oertel, W., *Biochem. Z.*, **60**, 480 (1914); *J. Chem. Soc.*, **106** (ii), 321 (1914).

[92] Suryanarayana, K., *J. Assoc. Maharajah's College, Vizianagaram*, **2**, 12 (1924); *Chem. Abs.*, **18**, 3548 (1924).

[93] Meiler, J. G., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **52**, 527 (1930).

[94] Krishnan, K. S., and Narayanaswamy, L. K., *Current Sci.*, **3**, 417 (1935); *Brit. Chem. Abs.*, **A**, 682 (1935).

Mack[95] has stated that chlorates may be electrolytically oxidized to perchlorate in an acid solution in the presence of oxygen activated by ultraviolet rays.

Fluorine Oxide. This compound absorbs ultraviolet light, but according to v. Wartenberg and Klinkott[96] is not decomposed by it. Palmer[97] finds that light from a hydrogen discharge tube on passing through a fluorite window into air at atmospheric pressure, caused the formation of a film on the outside of the window and upon this film a white powder. The film with metallic luster is soluble in alcohol and is probably calcium oxyfluoride. The powder, which forms more rapidly in moist air, is insoluble in water, but soluble in dilute hydrochloric acid.

COMPOUNDS OF NITROGEN

Ammonia. Pure liquid ammonia begins to absorb at about 2500A, the absorption increasing rapidly and being complete at about 2350A. The absorption also increases as the temperature rises, the threshold for absorption changing from 2320A at −78° to 2580A at 26°C. In aqueous solutions absorption increases with concentration, but is always less than that of the same number of ammonia molecules in the liquid or gaseous state.[98]

No reaction occurs when pure liquid ammonia is exposed to the wave-length 2300A, although this radiation is capable of causing the decomposition of gaseous ammonia.[99] Similarly, in water solution, the yield is kept low by recombination in triple collisions of the dissociation products H and NH_2 with the solvent molecules.

Kuhn[100] states that when ultraviolet rays of wave-lengths 2025 to 2140A fall on the compound $2AgCl.3NH_3$, the ammonia is decomposed.

The irradiation of solutions of alkali metals in liquid ammonia causes a reaction producing the amide ion and hydrogen.[101] The quantum efficiency is a function of both the metal concentration and the wave-length. There is a definite long wave-length threshold at about 2600A and a maximum quantum efficiency at about 2300A. The absorption is similar to that of liquid ammonia. In solutions of the alkali metals, the metal is almost completely dissociated into positive ions and solvated electrons. If the electron collides with the amide radical (produced by photodissociation) before the latter recombines with the hydrogen atom, an amide ion results and the hydrogen then has a greater opportunity to combine with another hydrogen atom. Since the probability that an amide radical will collide with electrons increases with the concentration of the latter, the quantum efficiency should be expected to increase regularly with the concentration, starting at zero and approaching unity asymptotically. This was found to be the case. Since the positive ion plays no essential part in the process, the quantum efficiency should be independent of the nature of the metal. This was true except for deviations encountered with caesium.

The amides of sodium and potassium show very strong continuous absorption throughout the ultraviolet with a maximum near the long wave-length thresholds of 3800-3900A for sodium, and 3950-4150A for potassium, amide. The absorption of light by the electron-ammonia complex, being photochemically inactive, lowers the quantum efficiency and accounts for the final yield being less than unity. This work gave a direct method of detecting the NH_2 radical as one of the products of the photodissociation of ammonia. From thermal considerations and the absorption of the metal amides, it appeared that sodium amide is optically dissociated into a normal state sodium atom and a normal state amide radical and is, therefore, ionically bound.

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[95] Mack, E. L., *J. Phys. Chem.*, **21**, 238 (1917).

[96] v. Wartenberg, H., and Klinkott, G., *Z. anorg. allgem. Chem.*, **193**, 409 (1930). See also Glissman, A., and Schumacher, H. J., *Z. physik. Chem.*, **B24**, 328 (1934).

[97] Palmer, F., Jr., *J. Chem. Physics*, **2**, 296 (1934).

[98] Briot, A., and Vodar, B., *Compt. rend.*, **201**, 500 (1935).

[99] Ogg, R. A., Jr., Leighton, P. A., and Bergstrom, F. W., *J. Am. Chem. Soc.*, **55**, 1754 (1933).

[100] Kuhn, W., *Compt. rend.*, **177**, 956 (1923); *Chem. Abs.*, **18**, 789 (1924); *J. chim. Phys.*, **23**, 521 (1926).

[101] Ogg, R. A., Jr., Leighton, P. A., and Bergstrom, F. W., *J. Am. Chem. Soc.*, **55**, 1754 (1933).

Fearon and M'Kenna[102] state that urea is produced by exposing ammonium carbonate to rays of wave-lengths 2000 to 2500A. The yield is thought to be increased in the presence of malachite green.

In the presence of oxygen or air, solutions of ammonia are oxidized to nitrites when exposed at 35° to 50°C. for three to nine hours to the radiations of a mercury arc.[103] Nitrates were not formed. Ammonium salts were also oxidized to nitrites, the reaction being slower in the case of the sulfate and chloride than in that of the carbonate. Corbet[104] finds hyponitrous acid to be formed as an intermediary product. Gion[105] claimed to have observed the formation of some nitrate in ammonia solutions exposed in quartz vessels to the radiations of a mercury arc. The oxidation proceeded faster at lower temperatures. He claimed also that if only the oxygen in contact with the ammonia solutions and not the solution itself, were irradiated there was oxidation by the ozone formed in the gas. The reaction was said to be sensitized by zinc or titanium oxides.

According to Baur and Renz,[106] ammonia is oxidized to nitrate, and oxalic acid to carbon dioxide on illumination when these substances are adsorbed on thallous chloride. The latter is itself converted to the photochloride.

The acceleration of the photochemical oxidation of ammonia by natural or artificial humus substances[107] or by various catalysts, such as titanium dioxide, alumina or zinc oxide present in soil, has been the subject of many observations, particularly by Indian chemists.[108] Most of these workers believe that ammonium salts are converted through nitrites to nitrates by sunlight in soils under the influence of sensitizers, but some also believe that various organic nitrogen compounds, including urea, amino-acids and uric acid, may similarly yield nitrites and nitrates.

Other workers tend to minimize the importance of photochemical processes in the soil. Fraps and Sterges[109] found that in a large group of samples with different ammonium salts, on the average 5 per cent of the ammonia was oxidized in the sunlight and 41 per cent in the dark. In all cases with corresponding bacterial cultures, those in the dark were oxidized more completely than those in the light. In sterile soils there was no evidence of nitrification. Nitrites in small amounts were found in cultures exposed to light, but little or none in those kept in darkness. This was taken to indicate that the nitric organisms are less resistant to light than are the nitrous organisms. A few non-sterile cultures of soil treated with ammonium salts and exposed to sunlight contained slightly more nitrate and nitrite than did the corresponding soils kept in darkness. These small increases were, however, attributed to differences in bacterial activity rather than to photonitrification. These authors did not regard their work as eliminating the possibility of photonitrification, but thought that photonitrification has a relatively slight effect upon soil processes.[110]

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[102] Fearon, W. R., and M'Kenna, C. B., *Biochem. J.*, **21**, 1087 (1927).

[103] Kuhn, W., *Compt. rend.*, **152**, 522 (1911).

[104] Corbet, A. S., *Biochem. J.*, **28**, 1575 (1934); **29**, 1086 (1935); Gion, L., *Compt. rend.*, **196**, 344 (1933).

[105] Gion, L., *Compt. rend.*, **195**, 421 (1932).

[106] Baur, E., and Renz, C., *Helv. Chim. Acta*, **15**, 1085 (1932).

[107] Zolcinski, J., *Rocz. Nauk Rolniczych*, **10**, 311 (1923); *Chem. Zentr.*, **96**, I 1123 (1925)

[108] Dhar, N. R., Bhattacharya, A. K, and Biswas, N. N., *Soil Sci*, **35**, 281 (1933); Rao, G. G, *Soil Sci.*, **38**, 143 (1934); Dhar, N. R., and Tandon, S. P., *J. Indian Chem. Soc*, **13**, 180 (1936); *Brit. Chem. Abs.*, **A**, 808 (1936); Sarkaria, A. R., and Fazal-Ud-Din, *Indian J. Agr. Sci.*, **3**, 1057 (1933); **5**, 195 (1935); Desai, S. V., and Fazal-Ud-Din, *Ibid.*, **6**, 777, 985 (1936); Dhar, N. R., and Mukerji, S. K., *J. Indian Chem. Soc.*, **12**, 756 (1936); **13**, 23, 535 (1936), Dhar, N. R., Tandon, S P., and Mukerji, S. K., *Ibid.*, **12**, 67 (1935); Osugi, S., and Aoki, M., *J. Sci. Soil Manure (Japan)*, **10**, 11 (1936); *Chem. Abs.*, **30**, 3029 (1936). Dhar has summarized his work on the influence of light on nitrogen fixation in soils in *Proc Natl. Acad. Sci. India*, **6**, Business matters, 3, 289 (1936); *Chem Abs.*, **31**, 6392, 6393 (1937); see also Dhar, N. R., Mukerji, S. K., Seshacharyulu, E. V., and Tandon, S. P., *Proc. Natl. Inst. Sci. India*, **3**, 75 (1937); *Chem. Abs.*, **32**, 1840 (1938).

[109] Fraps, G. S., and Sterges, A. J., *Soil Science*, **39**, 85 (1935); *Chem. Abs.*, **29**, 4867 (1935).

Nitrites. Sodium nitrite absorbs between 3000 and 4000A.[111] In 2-per cent aqueous solution in a glass cell, the nitrite almost completely absorbs the 3660A line. Although Berthelot and Gaudechon[112] had claimed nitrogen to be evolved as a result of the insolation of ammonium nitrite, Holmes[113] was unable to detect any loss of nitrite from a 2.5*N* solution of ammonium nitrite exposed in a quartz vessel for six hours to a 110-volt quartz mercury arc at a distance of 8-16 cm.

Nitrous acid can, however, be decomposed. Mukerji and Dhar[114] found the velocity coefficients in both the light and dark reactions

$$3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$$

to increase slowly with increasing concentrations of nitrous acid. The velocity was markedly accelerated by light, especially when closed vessels were used. Also, the velocity is proportional to the cube root of the light intensity, according to Murty and Dhar,[115] who employed the wave-lengths 4725, 5650, 7304 and 8500A. The temperature coefficient is less than unity and the Einstein law does not apply.

The influence of light upon the reaction between iodine and potassium nitrite has been studied by Berthoud and Berger.[116] The overall reaction is $KNO_2 + I_2 + H_2O \longrightarrow KNO_3 + 2HI$. In blue light the temperature coefficient is 1.30 between 35° and 45°C. The quantum yield is low, 22 quanta being required to cause one molecule of iodine to react in a solution containing 0.1 mole of potassium iodide and 1 mole of nitrite.[117] In the case of sodium nitrite, the quantum yield varies from 0.005 to 0.1 in phosphate buffers. The yield is independent of the pH, initial concentration of iodine, and rate of absorption of energy (4360A, 5460A, 5790A), but depends on the wave-length, temperature and concentrations of nitrite and iodine atoms. Also, the quantum yield decreases with increasing ionic strength.[118]

Nitrates. The absorption of light by the nitrate ion has been much studied.[119] It consists of two broad bands with maxima at 3100 and at about

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[110] See also Corbet, A. S., *Trans. Third Intern. Congress Soil Sci., Oxford*, **1**, 133 (1935); Waksman, S. A., Madhok, M. R., and Hollaender, A., *Soil Sci.*, **44**, 441 (1937); *Chem. Abs.*, **32**, 1376, 2670 (1938); Nath, B. V., *Sci Repts. Imp. Agr. Research Inst. New Delhi*, 98 (1937); *Chem. Abs.*, **32**, 4265 (1938); Joshi, N. V., and Biswas, S. C., *Trans Third Intern. Congr. Soil Sci., Oxford*, **3**, 104 (1935); *Chem. Abs.*, **32**, 5567 (1938).

[111] Weber, K., *Chem. Ztg.*, **56**, 642 (1932); *Phot. Korr.*, **66**, 317 (1930).

[112] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **152**, 522 (1911).

[113] Holmes, M., *J. Chem. Soc*, 1898 (1926).

[114] Mukerji, B. K., and Dhar, N. R., *Z. Elektrochem.*, **31**, 255 (1925).

[115] Murty, K. S., and Dhar, N. R., *J. Indian Chem. Soc.*, **7**, 985 (1930); *Chem. Abs.*, **25**, 2921 (1931).

[116] Berthoud, A., and Berger, W. E., *Helv. Chim. Acta*, **11**, 354 (1928); *J. chim. phys.*, **25**, 542 (1928).

[117] It was pointed out that previous work by Mukerji, B., and Dhar, N., [*Z. Elektrochem.*, **31**, 621 (1925)] was in error because of the use of an unsuitable analytical method.

[118] Durrant, G. G., Griffith, R. O., and McKeown, A., *Trans. Faraday Soc*, **34**, 389 (1938).

[119] Scheibe, G., *Ber.*, **59**, 2616 (1926); Morton, R. A., and Riding, R. W., *Proc. Roy. Soc.*, **113A**, 717 (1927); von Halban, H., and Eisenbrand, J., *Z. wiss. Phot.*, **25**, 149 (1928); Ley, H., and Volbert, F., *Ibid.*, **23**, 41 (1925); *Z. physik. Chem.*, **130**, 308 (1927); Eeckhout, J., *Naturw. Tijdschr.*, **17**, 72 (1935).

2060A, separated by a minimum at about 2600A. Krishnan and Guha[120] attribute the longer wave-length maximum to dissociation into nitrite ion and an oxygen atom and the second band to a similar dissociation producing an excited oxygen atom. Morton and Riding found that at concentrations greater than $0.025N$, Beer's law fails, the band shifting in the direction of higher extinction coefficients, due to a superposed band which alone is present when very concentrated solutions are employed. Hantzsch and others have found that in concentrated nitric acid or in dilute solutions of nitric acid or alkyl nitrates in ether the band at 3100A is replaced by one at 2700A. This has been said to represent the absorption of a "pseudo-acid" form of nitric acid.[121]

Baudisch and Mayer[122] observed that when aqueous solutions of potassium nitrate are exposed in a flat dish to the rays of a mercury lamp, oxygen is liberated, a blue coloration from starch and potassium iodide being produced in five to ten seconds. The interposition of a glass plate delays the change for twenty minutes. Warburg[123] made the first liquid-phase quantum yield determinations of the change of nitrates to nitrites. Since he observed that the photolysis proceeds much more rapidly in slightly alkaline than in neutral or in acid solutions, he employed solutions 0.00033 molar in sodium hydroxide. (This effect of pH was less apparent when more concentrated nitrate solutions were used.) In 0.33 molar potassium nitrate solutions the values of the quantum yield were 0.25 at 2070A, 0.17 at 2530A and 0.024 at 2820A. That the yields were low he explained by assuming that the efficiency of the dissociation is in some manner affected by the solvent. The fact that the yield decreases with increasing wave-length is readily interpreted by assuming that dissociation by larger quanta endows the dissociation products with sufficient kinetic energy to enable them more effectively to resist the imprisoning effect of surrounding solvent molecules which would tend to lower the quantum yields by inducing a recombination. Warburg also observed that for a given wave-length the quantum yield decreases with the concentration of the nitrate.

Anderson,[124] however, attempted to account for the low yields on the assumption that a reverse reaction may also occur, a "steady state" being reached when only a small portion of the nitrate had been decomposed. He supported this with the statement that the addition of small quantities of potassium nitrite partly or completely inhibited the photolysis of the nitrate Villars[125] and also Vogels[126] found no evidence for the existence of a "steady state" in this reaction. The decomposition maintains a linear rate for at least 480 minutes. Warburg calculated on the basis of the then available thermochemical data that the energy required to split an oxygen atom from the nitrate ion corresponds to a wave-length between 2800 and 3150A. The observations of Villars and of Warburg (Figure 114) indicate, however, that the drop in quantum yield occurs at a wave-length corresponding to a quantum much larger than that just required to effect the decomposition. The explanation is probably to be found in the detailed mechanism of the recombination processes which occur in aqueous solution. Villars had difficulty in accounting for the fact that measurable quantum yields could be obtained by the use of the wave-length 3350A, which he believed not to possess the requisite energy for dissociation. This difficulty has been removed by a more accurate knowledge of the heat of dissociation of oxygen, which makes the present value of the energy required for the decomposition correspond to about 3500A.[127] Villars also made more precise the data on the effect of pH. In either polychromatic or monochromatic light of 2537A the rates of decomposition increased at pH values slightly above 9 to maxima between 9 and 10, followed by relatively slight decreases at higher pH values. Vogels observed that the pH falls during photolysis, and that the rate may be accelerated by tartrates or, after a delay, by manganous salts.

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[120] Krishnan, K. S., and Guha, A. C., *Current Sci.*, **2**, 476 (1934); *Chem. Abs.*, **28**, 6370 (1934); *Proc. Indian Acad. Sci.*, **1A**, 242 (1934); *Chem. Abs.*, **29**, 1326 (1935).

[121] See also Siegler-Soru, E., *Compt. rend.*, **183**, 1038 (1926). For absorption of the crystals, see Rodloff, G., *Z. Physik.*, **91**, 511 (1934).

[122] Baudisch, O., and Mayer, E., *Ber.*, **45**, 1771 (1912); Baudisch, O , and Benford, F., *Naturwiss.*, **24**, 361 (1936).

[123] Warburg, E., *Sitz. Preuss. Akad. Wiss. Math. phys. Klasse*, 1228 (1918); *Chem. Abs.*, **14**, 1930 (1920); *Z. Elektrochem.*, **25**, 334 (1919).

[124] Anderson, W. T., Jr., *J. Am. Chem. Soc.*, **46**, 797 (1924).

[125] Villars, D. S., *J. Am. Chem. Soc.*, **49**, 326 (1927).

[126] Vogels, H., *Bull. sci. acad. roy. Belg.*, **22**, 320 (1936); *Chem. Abs.*, **30**, 6650 (1936); *Brit. Chem. Abs.*, **A**, 687 (1936).

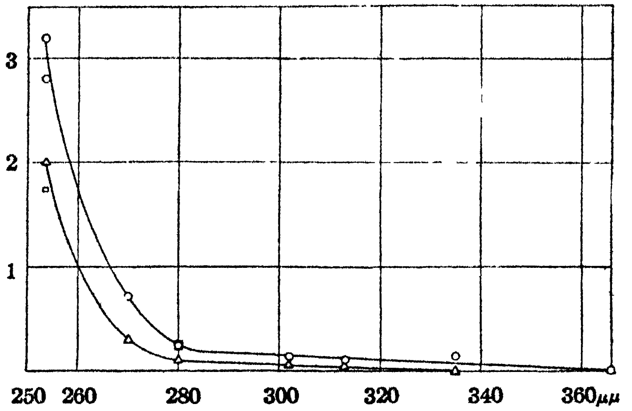

FIGURE 114. Quantum Efficiency of Monochromatic Light Absorbed by M. KNO_3. ○ = $\phi \times 10$ (buffered, pH 9.9). △ = $\phi \times 10^2$ (unbuffered, pH 5.8). □ = $\phi \times 10$ (Warburg, KNO_3 0.33 M, NaOH 0.0003M) where ϕ = moles transformed per quantum absorbed (Villars, *Journal American Chemical Society*).

Cultrera[128] finds that with mercury lamp irradiation, the reduction of nitrates may proceed to the formation of ammonia.

The decomposition of nitrate crystals appears to be confined to a surface layer not more than 20μ thick. At greater depths, recombination appears to be complete, since the oxygen cannot escape. Polarized rays with vibrations along the normal to the plane of the nitrate ions are much less effective than those with vibrations in the plane of the ions. In crystals, the wave-length threshold is much shorter, 2500A.[129]

Mercury nitrate also undergoes a photochemical change in aqueous solution, the sensitivity of the nitrate being increased by addition of alcohol or glycerol.[130] Fazal-ud-Din[131] has stated that the reduction of solutions of a number of nitrates

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[127] Note also Hymas, F. C., *J. Soc. Chem Ind*, **50,** 193T (1931)

[128] Cultrera, R, *Gazz. chim. ital*, **66,** 440 (1936); *Chem. Abs.*, **31,** 3389 (1937); *Ann. staz. sper. agrar. Modena,* **5,** 163, 175 (1936); *Chem. Abs.*, **32,** 3266 (1938).

[129] Krishnan, K. S., and Narayanaswamy, L. K., *Current Sci.*, **3,** 417 (1935); *Brit. Chem. Abs.*, **A,** 682 (1935); *Trans. Faraday Soc.*, **31,** 1411 (1935).

[130] Shljivic, S., and Nicolic, D., *Bull. soc. chim. roy. Yougoslav,* **6,** 159 (1936); *Chem. Abs.*, **30,** 4761 (1936); *cf.* Mudrovcic, M., *Bull. soc. chim roy. Yougoslav.*, **7,** 41 (1936).

[131] Fazal-ud-Din, *Indian J. Agr. Sci.*, **6,** 844 (1936); *Chem. Abs.*, **30,** 8493 (1936); see also Rao, G. G., and Murty, K. S., *Proc. Natl. Inst. Sci. India,* **3,** 133 (1937); *Chem. Abs.*, **32,** 2028 (1938).

(1 mg. per cc.) can be brought about by sunlight although ultraviolet is more effective. This is in line with the data of Villars. Decomposition is said to be increased by the presence of reduced nickel or carbohydrates, but not to occur in the presence of zinc oxide.

The oxides N_2O_5, TeO_3 and MoO_3 exhibit two regions of continuous absorption separated by a band of transmitted radiation.[132] The first band, in each case, is interpreted as resulting from the separation of an oxygen atom in the ^3P state from the molecule, and the second as resulting from the separation of an oxygen atom in the metastable ^1D state. From the absorption of N_2O_5 the heat of dissociation of oxygen could be calculated to be 128 kcal, not far from the correct value of 117 kcal.

Other Nitrogen Compounds. That commercial sodium cyanide made from calcium cyanamide develops color in light and bleaches in darkness is attributed by Buchanan and Barsky[133] to a reversible photochemical reaction between cyanamide and a ferrocyanide, the latter being a contaminant.

Crystalline sodium azide is decomposed by wave-lengths below 4050A, the rate being directly proportional to the intensity.[134] The threshold for decomposition by bombardment with electrons lies at 11.65 volts. Obviously, no relation between these two thresholds is apparent.

Muraraour[135] obtained only negative results in studying the effects of ultraviolet light, the alpha-rays from polonium, and x-rays on nitrogen iodide, picric acid, lead picrate, trinitrotoluene, nitrocellulose, nitroglycerin and *sym.*-diethyldiphenylurea.[136]

COMPOUNDS OF SULFUR

Exposure of a quartz reaction vessel containing sulfur, water and air to ultraviolet radiation results in the formation of various oxygen acids of sulfur. Dubrisay and Pallu[137] believe pentathionic acid to be the first product formed; this then slowly undergoes decomposition yielding sulfuric acid, sulfurous acid, sulfur and hydrogen sulfide.

The photochemical reaction between yellow arsenic and sulfur dissolved in carbon disulfide results in the formation of insoluble sulfides whose properties differ from those of known sulfides or of a mixture of the elements.[138]

By irradiating mixtures of carbon disulfide and carbon tetrachloride in a Vitaglass screened mercury vapor lamp, Doran and Gillam[139] obtained a polymer of carbon monosulfide as a reddish-brown solid. Nicholes, Simmons and Crockford,[140] state that carbon disulfide is not decomposed by the 3660A line, but that the 2537A line, or a mercury arc in Pyrex leads to the formation of decomposition products including $(CS)_x$, C_3S_2 and a yellowish-brown solid $(C_3S_2)_x$.[141]

Sulfur dichloride absorbs strongly all wave-lengths shorter than 6200A. The monochloride shows a strong maximum at 2660A.[142] The photochemical reaction between sulfur monochloride and chlorine has an induction period which may be lessened by substituting sunlight for diffused daylight. The rate of reaction is also greater in sunlight. The reaction may be catalyzed by antimony pentachloride.[143] Sulfur dichloride is one of the final products of the dissociation of sulfur monochloride by the action of light, S_8Cl_4 being an intermediate product.[144] When sulfur dichloride is heated or irradiated it undergoes changes in density, the course being that of a first order reaction. The velocity of reversion after irradiation is higher than after displacement by heat, probably because of the formation of a catalyst by the action of light.

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[132] Dutta, A. K., and Gupta, P. K., *Proc. Roy. Soc.*, **139A**, 397 (1933).

[133] Buchanan, G. H., and Barsky, G., *Z. angew. Chem.*, **44**, 383 (1931).

[134] Müller, R. H., and Brous, G. C., *J. Chem. Physics*, **1**, 482 (1933).

[135] Muraraour, H., *Bull. soc. Chim.*, **53**, 612 (1933).

[136] Mada, T. [Japanese P. 101,815, July 1, 1933], claims to prepare a nonhygroscopic sodium bicarbonate by raying with ultraviolet for about twenty minutes.

[137] Dubrisay, R., and Pallu, R., *Compt. rend.*, **193**, 339 (1931). See also Calcagni, G., *Gass. chim. ital.*, **65**, 558 (1936); *Chem. Abs.*, **30**, 384 (1936).

[138] Haenny, Ch., *Helv. Chim. Acta*, **13**, 725 (1930); *Chem. Abs.*, **25**, 643 (1931).

[139] Doran, W., and Gillam, A. E., *J. Soc. Chem. Ind.*, **47**, 259T (1928).

[140] Nicholes, P. M., Simmons, N. L., Jr., and Crockford, H. D., *J. Elsiha Mitchell Sci. Soc.*, **52**, 51 (1936); *Chem. Abs.* **30**, 7457 (1936).

[141] For the absorption spectrum of carbon disulfide, see Bruhat, G., and Pauthenier, M., *Compt. rend.*, **181**, 104 (1925); *J. Phys. Radium*, **6**, 287 (1925).

Hydrogen Sulfide. Solutions of hydrogen sulfide in water and hexane have, according to Ley and Arends,[145] practically the same absorption curve, the maximum, at 1890A, being attributed to undissociated molecules. Absorption at 2270A in aqueous solutions was attributed to the HS^- ion. Warburg and Rump [146] found differences in the absorption curves in these solvents. Warburg found that in hexane the quantum yield for decomposition of hydrogen sulfide is 0.97 at 2070A, 0.95 at 2220A and 0.96 at 2530A, the concentrations being 0.251, 0.1355 and 0.0452 molar. In aqueous solutions, however, the values were much lower, being 0.43 at 2070A for 0.015 and 0.32 for 0.0369 molar solutions. At 2220A, the yield was 0.32 and at 2530A 0.22. Warburg pointed out that the difference might be due to the fact that hydrogen sulfide does not react with hexane but does react with water. He believed it possible to apply the Einstein law to solutions in which there is no interaction between photolyte and solvent but not to those in which there is such an interaction. An analysis from the standpoint of the influence which might be exerted by hydrated or solvated ions upon the recombination processes subsequent to the primary process does not seem to have been made as yet.

Sulfites. Albu and Goldfinger [147] have studied the absorption of the sulfite ion on the basis of the Franck-Haber theory of the electron-affinity spectrum of ions. Within the range 5000 to 1950A the absorption spectrum depends only upon the pH and concentration of the solutions, and not on their age or method of preparation, provided autoxidation is prevented. The absorption of dissolved undissociated sulfur dioxide can be observed at pH 4 or lower. Absorption begins at 3270A and has a maximum at 2800A. The spectrum of the sulfite ion SO_3'', a structureless electron-affinity spectrum, may be observed in solutions of pH greater than 6. The sulfite ion spectrum has a long wave-length limit of 2660A and corresponds to the process:[148] $SO_3^{--}(H_2O) + h\nu \rightarrow SO_3^- + H + OH^-$. The Franck-Haber theory predicts that the corresponding electron-affinity spectrum of the bisulfite ion should be 1.5 to 2 e-volts to the short wave-length side of that of the sulfite ion. In agreement with this prediction, there was found to be no absorption by the bisulfite ion at wave-lengths greater than 2250A. The long wave-length limits of the absorption by the $S_2O_8^{--}$ and $S_2O_6^{--}$ ions are 2700 and 2600A, respectively. No absorption by the sulfate ion could be detected. Haber and Wansbrough-

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[142] Lowry, T. M., and Jessop, G., *J. Chem. Soc.*, 1421 (1929); Lorenz, L., and Samuel, R., *Z. physik. Chem*, **14B**, 219 (1931).

[143] Bothamley, R. P., *Trans. Faraday Soc.* **24**, 47 (1928)

[144] Spong, A. H., *J. Chem. Soc.*, 485 (1934).

[145] Ley, H., and Arends, B., *Z. physik. Chem.*, **15B**, 311 (1932).

[146] Warburg, E., and Rump, W., *Z. Physik*, **58**, 291 (1930). Studies in dichloromethane, chloroform and carbon tetrachloride as solvents are due to Avery, W. H., and Forbes, G. S., *J. Am. Chem. Soc.*, **60**, 1005 (1938).

[147] Albu, H. W., and Goldfinger, P., *Z. physik. Chem.*, **16B**, 338 (1932).

[148] See for another interpretation, Farkas, L., and Farkas, A., *Trans. Faraday Soc.*, **34**, 1113 (1938).

Jones[149] have studied the photochemical reaction which (in the absence of oxygen) occurs subsequent to the primary process postulated above. As secondary reactions there might be expected a combination of the hydrogen atoms to molecular hydrogen and a combination of two SO_3^- ions into a dithionate ion $S_2O_6^{--}$. The quantum yields were, however, very small for the formation of dithionate ions, being about 0.07 at pH 9 and decreasing at greater alkalinities. Instead, the majority of the SO_3^- ions formed in the primary process combine with hydrogen atoms to form bisulfite ions.

In the presence of air, ultraviolet (2300-2800A) accelerates the thermal oxidation of sodium sulfite. A 0.2*N* solution of sodium sulfite is completely oxidized in light in about three hours. A particularly interesting feature is the inhibiting effect of small quantities of various substances. According to Mathews and Dewey[150] pyridine strongly inhibited the process when present in the concentration of 5 cc. per liter. Methyl and ethyl acetate had a much weaker effect. Five drops of benzaldehyde per liter strongly inhibited the reaction but the same amount of glycerol produced only a slight effect. Urea had no effect. Hydroquinone and phenol were effective but not as much so as quinine sulfate. Sucrose (0.025*N*) produced less inhibition than did phenol (0.001*N*).[151]

Bäckström[152] reported a series of investigations on the behavior of inhibitors, particularly alcohols, which did much to explain the nature of the photochemical oxidation and of the thermal one as well. It was shown that the photochemical process is a chain reaction, the quantum yields in the absence of inhibitors corresponding to an uptake of about 50,000 molecules of oxygen per quantum absorbed. Since in general, the inhibitors of the photochemical reaction also inhibited the thermal one, it followed that the latter was a chain reaction as well. The role of the inhibitor in both cases consists in the breaking of chains, probably by an induced reaction between the inhibitor and one of the reactants. Attention was devoted to the mechanism of the inhibition and to the length of the chains when broken rather than to the nature of the chains, since the work was done before the theory of the electron affinity spectrum had been developed.

The rates of the light and dark reactions could be represented by the formulas:

$$V_{\text{light}} = k_3 v_{\text{dark}} \text{ and } V_{\text{dark}} = \frac{k_1}{kC + k_2}$$

in which k_1, k_2 and k_3 are constants applicable to all alcohols as inhibitors, k is a specific constant for each inhibitor and C is the concentration of the inhibitor. The form of the equations suggested that the presence of the alcohols did not affect the rate of starting the chains so that the inhibitors function solely by breaking the chains. The constant k_2 indicates that some chains may be broken by processes independent of the presence of added inhibitor. In the case of the thermal reaction it was shown that the alcohols were oxidized in breaking the chains. The amount of oxidation of alcohols could be determined by colorimetric measurements of the aldehydes and ketones produced. At low inhibitor concentrations the amount of alcohol oxidized increases with increasing alcohol concentration. At high inhibitor concentrations the amount of alcohol oxidized per unit time is constant, and independent of concentration, in either the thermal or photochemical oxidation. Over a considerable range of high inhibitor (isopropyl alcohol) concentrations, the product of the rate of sulfite oxidation and inhibitor remained constant, and the ratio between this product and the amount of acetone formed was the same, 74 to 77, in the thermal and in the photochemical oxidations. From this it followed that in a solution of a given composition the chain length is the same whether the chains are formed thermally or photochemically.

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[149] Haber, F., and Wansbrough-Jones, O. H., *Z. physik. Chem.*, **18B**, 103 (1932).

[150] Mathews, J. H., and Dewey, L. H., *Eighth Intern. Congr. Appl. Chem., Sect. IX, Orig. Comm.*, **20**, 247 (1912); *J. Am. Chem. Soc.*, **39**, 635 (1917).

[151] Mathews, J. H., and Mason, R. B., *J. Phys. Chem.*, **30**, 414 (1926) later erroneously stated the phenols to act as positive catalysts.

[152] Bäckström, H., *J. Am. Chem. Soc.*, **49**, 1460 (1927); *Medd. Kgl. Vetenskapsakad. Nobelinst.*, **6**, No. 16 (1927); Bäckström, H., and Alyea, H. N., *J. Am. Chem. Soc.*, **51**, 90 (1929).

A solution 0.1*M* with respect to benzyl alcohol gave a quantum yield of 64 molecules of oxygen or 128 of sulfite reacting per quantum. From the amount of acetone formed it was determined that the number of molecules of sulfite oxidized for each molecule of alcohol oxidized was 58, of the same order of magnitude. This indicates that in the process of breaking a reaction chain, 2.2 molecules of the alcohol are oxidized. In other words, the induced oxidation of benzyl alcohol has a quantum yield of 2.2. It was later found by Bäckström[153] that light intensity enters into the rate equation as approximately the half power, both in the numerator and in an additional term in the denominator. The reaction had a pH dependence which suggested that both sulfite and bisulfite ions must be concerned in the mechanism. When oxidation occurs, the primary SO_3^- probably forms an intermediary SO_5^- ion which dehydrogenates the bisulfite ion, present at the effective pH, producing a sulfate ion and reforming the SO_3^- ion which can again be oxidized. The inhibiting action of the alcohol is due to its induced oxidation, probably by the assumed SO_5^- ion.

Allmand and Maddison[154] believed that light of ordinary wave-lengths has no effect on the rate of oxidation of sodium sulfite in solution. Titoff[155] found that copper sulfate is without effect upon the ultraviolet reaction, but catalyzes the reaction in ordinary light. Franck and Haber[156] postulate that the effect of the copper ion is to start the thermal reaction by forming the ion SO_3^- the same ion as that later found by Bäckström to be the primary product in the photoreaction.[157]

Persulfates. That aqueous solutions of potassium persulfate are light-sensitive was demonstrated by Dhar[158] and Elbs and Neher.[159]

In a series of investigations, Morgan and Crist[160] found that the reaction could be expressed by the equation:

$$K_2S_2O_8 + H_2O \longrightarrow 2KHSO_4 + 1/2O_2$$

In very dilute solutions, the order of reaction was unimolecular, as is the thermal reaction which occurs at higher temperatures. In concentrated solutions which absorbed all the light, the reaction was of zero order. Increasing the oxygen concentration did not reverse the reaction. Hydrogen and nitrogen appeared to exhibit an accelerating effect. Potassium persulfate absorbs only wave-lengths shorter than about 2500A in a 0.01*M* solution and 3000A in a 0.1*M* solution. The upper limit of the radiations effective in producing the decomposition was probably at about 2900A and the maximum sensitivity at about 2300A. The reaction was proportional to the light intensity, and the temperature coefficient was 1.18, compared with about 3 for the thermal reaction. The rate of reaction was retarded by the addition of potassium hydroxide, potassium sulfate or sulfuric acid. The retardation was not due to internal filtering, was hyperbolic and seemed to be of the same general nature in the presence of various added electrolytes. The quantum efficiency was unity in 0.05 molar neutral or alkaline solutions, the wave-lengths used being 2540, 2650 and 3020A.[161] In acid solutions the values of the quantum yield are somewhat reduced. Solid potassium persulfate is also decomposed by ultraviolet light.

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[153] Bäckström, H., *Z. physik. Chem.*, **25B**, 122 (1934).

[154] Allmand, A. J., and Maddison, R. E. W., *J. Chem. Soc.*, 650 (**1927**).

[155] Titoff, A., *Z. physik. Chem*, **45**, 641 (1903)

[156] Franck, J., and Haber, F., *Sitzber. Preuss. Akad. Wiss.*, 250 (**1931**); see also Albu, H. W., and von Schweinitz, H. D., *Ber.*, **65B**, 729 (1932).

[157] There have from time to time been efforts to employ ultraviolet light in the preparation of sulfuric acid. Kühne, H., French P. 393.461, 1908; *J Soc. Chem. Ind.*, **28**, 90 (1909); British P. 17,520, 1908; *J. Soc. Chem. Ind.*, **28**, 982 (1909). German P. 203,541; Chmura, T., *Chem. Age*, **13**, 327,307 (1925); British P. 237,257; de Sotto, G. E., British P. 265,857, July 20, 1926. No practical applications have been made.

[158] Dhar, N. R., *Proc. Akad. Vetensk.*, **23**, 308 (1920).

[159] Elbs, K., and Neher, P., *Chem. Z.*, **45**, 1113 (1921).

[160] Morgan, J. L. R., and Crist, R. H., *J. Am. Chem. Soc.*, **49**, 16, 338, 960 (1927).

Marmier[162] has reported that decomposition of aqueous solutions of sodium thiosulfate results in the formation of sulfur and hydrosulfite. The latter was rapidly decomposed by ultraviolet and after an exposure of 75 minutes under the conditions of observation no traces remained.

Ammonium Thiocyanate. Holmes[163] observed that freshly prepared concentrated solutions of ammonium thiocyanate exposed to ultraviolet light in glass containers evolved a gas and developed a reddish color which soon faded. In quartz containers, sulfur separated from the solution. Werner and Bailey[164] suggested that the photoreaction involved only the production of ammonia and thiocyanic acid, the color being due to traces of iron as impurity. This theory was corroborated by Patten and Smith.[165] According to these investigators, light accelerates oxidation of the iron so that the latter can react with the thiocyanate. Wave-lengths less than 5400A produced the coloration, those between 4000 and 4300A being the most effective. Sharma[166] considered the color to be due to a loose additive complex of ferrous thiocyanate with oxygen.

Shorter wave-lengths (3000-1850A) can decompose thiocyanates of ammonium, sodium or potassium with liberation of sulfur, according to Jablczynski and Jablczynska.[167] The reaction is believed to be reversed in the dark.

The velocity of solution of amorphous selenium is increased by light but that of monoclinic selenium is not affected.[168]

ARSENIC AND ANTIMONY COMPOUNDS

An account of the investigations on the source of the glow of arsenic at high temperatures is beyond the scope of this work.[169] Lead arsenite is photosensitive. When dried in an air-bath in the dark, it remains white, but when exposed to light it turns brown. Mixed with gelatin and applied to paper and dried in the dark, it can be used in photography, developing warm sepia tones when exposed under a negative. Not all samples of lead arsenite possess this property. No other metallic arsenites are light-sensitive.[170]

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[161] Crist, R. H., *J. Am. Chem. Soc.*, **54**, 3939 (1932).

[162] Marmier, L., *Compt. rend.*, **154**, 32 (1912).

[163] Holmes, M., *J. Chem. Soc.*, 1690 (**1926**).

[164] Werner, E. A., and Bailey, K. C., *J. Chem. Soc.* 2970 (**1926**); more complicated theories of the origin of the color were suggested by Holmes, M., and by Bhatnagar, S., Dunnicliffe, H., and Ali, M., *J. Indian Chem Soc.*, **4**, 229 (1927).

[165] Patten, C. G., and Smith, H. D., *Trans. Roy. Soc. Canada*, **22**, 221 (1928).

[166] Sharma, B. S., *J. Chem. Soc.*, 308 (**1930**); see also Rao, S. V., *J. Chem. Soc.*, 880 (**1934**).

[167] Jablczynski, K., and Jablczynska, H., *Roczniki Chem.*, **10**, 579 (1930); *Chem. Abs*, **25**, 877 (1931).

[168] Shidei, J., Hashizuma, S., and Kitahara, S., *Bull. Chem. Soc. Japan*, **10**, 374 (1935); *Brit. Chem. Abs.*, **A**, 1331 (1935); Sterzel, S. E., and Afzelius, I., *Svensk Kem. Tidskr.*, **49**, 281 (1937); *Brit. Chem Abs.*, **A** (I), 90 (1938).

[169] Emeléus, H. J., *J. Chem. Soc.*, 783 (**1927**) For phosphorus, Emeléus, H. J., *Nature*, **115**, 460 (**1925**); *J. Chem. Soc.*, 1336 (**1926**); Emeléus, H. J., and Purcell, R. H., *J. Chem. Soc.*, 788 (**1927**); Petrikaln, A., *Naturwiss.*, **16**, 205 (1928); Miller, C. C., *J. Chem. Soc.*, 1823, 1829 (**1929**).

Detailed determinations have been made by Weigel[171] of the absorption of light and the electrical conductivity of realgar when the crystal is exposed to light of various wave-lengths. Fragments of realgar exposed to direct sunlight for 112 hours behind sheets of glass of various colors showed the greatest change with a green glass of maximum transparency near 520μ.

Solutions of antimony oxide in hydrochloric or tartaric acids and of antimony trichloride in saturated sodium chloride solution in ordinary glass vessels are photochemically oxidizable by sunlight.[172] Light of shorter wave-length is required in the case of solutions of antimony trioxide or of tartar emetic in sulfuric acid, or of antimony trichloride in carbon tetrachloride and in saturated calcium chloride solution. The amount of oxidation depends on the kind of solution, wave-length and intensity of the radiation and concentrations of antimony and of oxygen.

In carbon disulfide, white phosphorus is converted by light into red phosphorus, a dissociation and recombination being involved.[173]

When boron hydride, B_4H_{10}, is kept over mercury at room temperature, it slowly undergoes decomposition with the formation of the hydride, B_2H_6. The decomposition is accelerated greatly by ultraviolet rays, but not by sunlight.[174]

METALS AND SALTS

Under the influence of light, copper combines with chlorine[175] but not with bromine or iodine; with oxygen, but not with sulfur; with water, but not with hydrogen sulfide; with ammonia, but not with phosphine or arsine. Aqueous solutions of the chlorides or sulfates of gold, silver, uranium, copper, nickel, chromium and cobalt were reported by Berthelot and Gaudechon[176] to be unaffected by ultraviolet radiation. The sulfates of nickel and cobalt gave a slight brown precipitate, attributed to the presence of traces of iron. Solutions of ferrous sulfate gave a precipitate of the basic salt. Pure ferric sulfate did not give a precipitate but in the presence of nickel or cobalt sulfate precipitated the basic salt. Urbain and Scal[177] stated that the pasasge of rays (from an arc) through tetrachlorides of titanium, tin, or carbon, caused a marked decomposition, chlorine being liberated.

A method of depositing metals has been advocated by Jacquier.[178] The process comprises precipitating metals from solutions of their salts by treatment with ultraviolet rays in the presence of aluminum. Mercury vapor lamps are suspended between aluminum plates in the tank containing the solution to be treated.

Light is believed to facilitate the reduction of some metallic oxides. Actinic rays are said to promote the interaction of oxygenated compounds (*e.g.*, calcium phosphate), barytes or bauxite with chlorine in the presence of a reducing agent such as carbon. At temperatures between 200° and 1000°C., inorganic halides are said to be secured.[179]

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[170] Reissaus, G. C., *Z. angew. Chem.*, **44**, 959 (1931).

[171] Weigel, O., *Tech. Min. Petr Mitt.*, **38**, 288 (1925); *Chem. Abs.*, **20**, 3268 (1926)

[172] Brüll, W., with Schlagel, H., *Z. anorg. Chem.*, **217**, 401 (1934).

[173] Rathenau, G., *Physica*, **4**, 503 (1937), *Chem. Abs.*, **31**, 6560 (1937).

[174] Stock, A., and Friederici, K., *Ber.*, **46**, 1959 (1913).

[175] Berthelot, D., and Gaudechon, H., *Compt rend.*, **157**, 129 (1915)

[176] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **152**, 376 (1911).

[177] Urbain, E., and Scal, C., *Compt. rend.*, **168**, 887 (1919).

[178] Jacquier, G., British P. 17,790, Aug. 2, 1913.

The yellow amorphous modification of indium oxide is sensitive to light when in the presence of some reducing agents as benzaldehyde. The color of the oxide changes from gray to dark gray or black. Also, some reduction products are formed. Selenium oxide is not sensitive under the same conditions.[180]

Krauss and Gerlach[181] found that the preparation of iridium halides by the action of the halogens upon iridium or its hydroxide could be hastened by the action of light.

Hibben[182] observed that some large crystals of magnesia became tinted a deep purple on exposure to the 2537A line. On removal from the light, spontaneous decolorization occurred in several weeks at 25°C., or in three minutes at 1000°C. It was accompanied by emission of light throughout the visible spectrum. The first effect was ascribed to a type of electron migration, and the later effects to a recombination. It may be related to the presence of impurities since not all crystals behave alike. The 4358A line decolorized the purple crystals in thirty minutes.[183]

Light from a carbon arc accelerates the rate of evolution of hydrogen from dilute sodium and potassium amalgams in water.[184]

Iron Salts. That ferrous hydroxide and sulfate are more rapidly oxidized in light than in darkness was first made known by Chastaing.[185] The ferrous ion when irradiated with wave-lengths shorter than 2900A, is oxidized to ferric ion and hydrogen is evolved.

$$Fe^{++} + HOH + h\nu \longrightarrow Fe^{+++} + H + OH^-$$

The quantum yield in aqueous solution is 0.05. The primary process is followed by a combination of two hydrogen atoms, which occurs in competition with the reverse reaction. The activation energy of the latter is 7 kcal.[186]

The color of hydrochloric acid solutions of ferric chloride increases on exposure to sunlight or other sources of intense light.[187] On removal from the light, the solutions slowly return to their original condition. Increased light absorption also results from heating a solution of ferric chloride. A crystal of ferric chloride shows, in addition to general absorption starting at 5000A, a sharp band at 6200A, from 50 to 100A in width.[188]

In alcoholic solution, ferric chloride is readily bleached in light by reduction to the ferrous salt, a reaction discovered by Bestucheff in 1725.[189] The reaction is best conducted in the presence of organic substances, either as solvent or added to the solution, or bound in complex form to the iron, since these organic compounds can be oxidized by or react with the chlorine liberated in the photochemical decomposition. A wide variety of organic reducing agents have been studied, including paper, glycerol, and many acids. It was as a result of the study of this reaction that Grotthuss evolved the law which bears his name.[190] Winther[191] found that aqueous solutions of ferric chloride, when free from organic matter, undergo only a very slight reaction. Puxeddo[192] reported that the reaction in absolute ether follows a monomolecular course. At the end of reaction, the ether was partially chlorinated.

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[179] British P. 302,927, Dec. 22, 1927, to Naamlooze Vennootschap Elektrochemische Industrie; *Chem. Abs.*, **23**, 4304 (1929).

[180] Renz, C., *Helv. Chim. Acta*, **15**, 839 (1932); *Chem. Abs.*, **26**, 4754 (1932).

[181] Krauss, F., and Gerlach, H., *Z. anorg. allgem. Chem*, **147**, 265 (1925).

[182] Hibben, J. H., *Phys. Rev.*, **51**, 530 (1937).

[183] For effects of visible light and x-rays on lead oxides, see Hoffmann, J., *Z. anorg. Chem*, **228**, 160 (1936).

[184] Bhatnagar, S. S., Prasad, M., and Mukerji, D. M., *Quart. J. Indian Chem. Soc.*, **1**, 263 (1925); *Chem. Abs.*, **19**, 3429 (1925).

[185] Chastaing, P., *Ann. Chem.*, **10**, 145 (1877).

[186] Potterill, R. H., Walker, O. J., and Weiss, J., *Proc. Roy. Soc.*, **A156**, 561 (1936).

[187] Ritchie, K. S., *J. Phys. Chem.*, **32**, 1269 (1928).

[188] Rawlins, F., and Snow, C. P., *Z. Krist.*, **83**, 41 (1932).

[189] Plotnikow, J., "Algemeine Photochemie," p. 410. Berlin, de Gruyter, 1936.

Prasad and Sohoni[193] studied the influence of temperature, light intensity, water and neutral salts on the decomposition of ferric chloride in alcoholic solution. The temperature coefficient is 1.0 to 1.15. In anhydrous solution a steady state is apparently reached, the reaction being reversible. Small amounts of water increase the initial rate of the reaction but seem to decrease the total amount of reduction. Minute quantities of the chlorides of magnesium or the alkalies are strongly inhibiting. Variations of light intensity have a more pronounced influence on the rate of the reduction in dilute solutions than in more concentrated ones. The quantum yield varies from 0.6 to 4 in various alcohols, including methyl, ethyl, propyl and butyl.[194] The quantum yield increases with the concentration of the ferric chloride, the frequency of the light and the temperature. These workers find the products to be ferrous chloride and chlorine, no side reactions occurring within the first two hours. In later work, it was observed that in dilute solutions, two reactions may take place, each of zero order.[195] The initial velocity of the reduction in dilute solutions is proportional to a power of the concentration, which depends on the nature of the solvent. In concentrated solutions, however, the initial velocity is independent of the concentration of the ferric chloride. It was believed unlikely that the primary process involved a photodissociation.[196] There may be either an activation of ferric ions which then react with the alcohols, or an activation of a molecule of ferric chloride, which then reacts with a second molecule to yield ferrous chloride and chlorine, the latter attacking the alcohols. Either mechanism would give a quantum yield of two.

In studying the influence of light upon the decomposition of ferric iron preparations containing citric acid, a decomposition which sometimes causes the stoppers to be blown from bottles by the accumulation of carbon dioxide, Fry and Gerwe[197] reviewed the work on the reduction of ferric salts by organic acids in light. Eder[198] and de Vries[199] found ordinary light to effect the reduction of ferric salts in the presence of oxalic, citric and malic acids. A small amount of ferric chloride oxidized a great excess of acid. Neuberg[200] made an extensive study of the action of both sunlight and ultraviolet light upon sixty substances in the presence of ferric salts and uranic salts. Fry and Gerwe found that three moles of carbon dioxide were produced for each molecule of ferric sulfate reduced. No carbon monoxide formed. They proposed a mechanism in which the citric acid is converted into hydrogen, carbon dioxide and acetone-dicarboxylic acid. The latter immediately decomposed to yield a second molecule of carbon dioxide and acetoacetic acid, which in turn, yielded a third molecule of carbon dioxide and acetone. The ferric sulfate was believed to aid the oxidation of the hydrogen formed in the first reaction. The summation of the reactions gave the stoichiometrical ratio between ferric sulfate reduced and carbon dioxide produced which was found experimentally. It is to be noted that the sequence of events was stated to depend upon an action of the light directly upon the citric acid rather than upon the ferric salt. From the preceding discussion, it is evident, however, that in most cases in which ferric salts are photochemically reduced in the presence of organic matter, the light acts primarily upon the ferric salt. Lal and Ganguli [201] reported that the rate of reduction of ferric salts in the presence of a mercury arc as source was proportional to the light intensity. Reduction was strongly accelerated by traces of thorium, uranium, copper and zirconium salts.[202]

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[190] Ross, W. H., *J. Am. Chem. Soc.*, **28**, 790 (1906); Schneider, M., *Z. physik. chem. Unterricht.*, **39**, 271 (1927); Benrath, A., *Z. physik. Chem.*, **74**, 115 (1910); Ghosh, J. C., and Mitra, B. N., *J. Indian Chem. Soc.*, **5**, 191 (1928); *Chem. Abs.*, **23**, 21 (1929).

[191] Winther, C., *Z Elektrochem.*, **18**, 138 (1912); *Z. wiss. Phot.*, **11**, 60 (1912); **9**, 205 (1910).

[192] Puxeddu, E., *Gazz. chim. ital.*, **50**, 154 (1920); **52**, 229 (1922).

[193] Prasad, M., and Sohoni, N. V., *J. Indian Chem. Soc.*, **8**, 489 (1931); *Chem Abs.*, **26**, 378 (1932).

[194] Prasad, M., and Limaye, P. S., *J. Indian Chem. Soc.*, **10**, 91, 101 (1933); *Chem. Abs.*, **27**, 3882 (1933).

[195] Prasad, M, and Mohile, B. V., *Proc. Natl. Acad. Sci. India*, **6**, 261 (1936); *Chem. Abs.*, **31**, 1298 (1937).

[196] Prasad, M., Mohile, B. V., and Nigudkar, K. D., *J. Univ Bombay*, **5**, Pt. 2, 142 (1936); *Chem. Abs.*, **31**, 3790 (1937).

[197] Fry, H. S., and Gerwe, E. G., *Ind. Eng. Chem.*, **20**, 1392 (1928).

[198] Eder, J. M., *Monatsh.*, **1**, 755 (1880); *Ber.*, **14**, 1183 (1881).

[199] deVries, H., *Rec. trav. Chim.*, **3**, 365 (1884); *Chem. Zentr.*, **56**, 219 (1885).

[200] Neuberg, C., *Biochem. Z.*, **44**, 495 (1912).

Ferrocyanides and Other Complex Salts. A reversible color change occurs in solutions of potassium ferrocyanide in sealed tubes exposed to light. Only after months is there some precipitation of ferrous hydroxide.[203] Equilibrium conditions for a 0.25-per cent solution of potassium ferrocyanide in water are reached after an exposure of thirty minutes to an arc.[204] With exposures of sixty minutes, the percentage decomposition decreased from 0.23 per cent to 0.10 per cent as the concentration of the salt was decreased from 7.67 to 3.07 gm. per 100 cc. A further decrease in the concentration of the salt to 1.53 gm. per 100 cc. resulted in an increase in the decomposition to 0.40 per cent. Up to a certain amount, the presence of potassium hydroxide aids the decomposition, but larger amounts decrease decomposition to the value found for neutral solutions. Complete reversibility of the reaction was shown after the first exposure to light and darkness, but with successive equal exposures the amount of decomposition increased, and the reversibility of the reaction decreased. Baur [205] found oxygen to accentuate the darkening in color of ferrocyanide solutions on illumination, although darkening occurs also with deaerated freshly prepared solutions. In acid solutions, Prussian blue forms. If the ferrocyanide solution is passed through a column of granulated aluminum, the original yellow color disappears, and the solution ceases to be photochemically sensitive. These facts were interpreted as indicating that the ferrocyanide ion itself is photochemically insensitive, the light reaction being due to the photodecomposition of the ferricyanide ion always present in small quantities.

Baudisch [206] observed that ferrous ions, as well as pentacyanoaquoferrite ions, are produced when solutions of potassium ferrocyanide, neutral or feebly acid with carbonic acid, are exposed to the carbon arc or to direct sunlight in the absence of air. In the presence of air and light, the yellow ferrite ions are immediately oxidized to the dark violet pentacyanoaquoferrate ions, which react with the first named ions to form complex compounds that have a pale yellow color. The presence of sodium azide inhibits the formation of these products, and under these conditions the yellow potassium ferrocyanide is oxidized directly to the dark violet potassium pentacyanoaquoferrate ion. In an air-free system, the iron atom of potassium ferrocyanide is activated by light in consequence of the mobilization of its secondary valences. The original inactive compound is rapidly reformed in the dark. In the presence of air and light, peroxo-compounds possessing unusual oxidizing powers are produced in addition to the usual ferric and ferrous complex ions.

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[201] Lal, P., and Ganguli, P. B., *Z. anorg. allgem. Chem.*, **229,** 16 (1936).

[202] See also Burt, J. B., *J. Am. Pharm. Assn.*, **17,** 650 (1928) and Purkayastha, R. M, *J. Indian Chem. Soc.*, **9,** 237 (1932).

[203] Baudisch, O., and Bass, L., *Ber.* **55B,** 2698 (1922); *Chem. Abs.*, **16,** 4137 (1922) For the absorption spectra, see Plotnikow, J., and Karschulin, M., *Z. Elektrochem*, **33,** 212 (1927); Getman, F., *J. Phys. Chem.*, **32,** 187 (1928); Briggs, S., *J. Chem. Soc.*, **99,** 1019 (1911); **117,** 1026 (1920); *J. Phys. Chem.*, **32,** 1422 (1928).

[204] Rossi, G., and Bocchi, C., *Gazz. chim. ital.*, **55,** 876 (1925).

[205] Baur, E, *Helv. Chim. Acta*, **8,** 403 (1925).

[206] Baudisch, O., *Ber.*, **62B,** 2706 (1929).

Dickinson and Ravitz[207] state that systems containing the ferro- and ferricyanide ions together with the iodide ion and iodine, are sensitive to light not absorbed by the complex cyanides. When light was directed into such an equilibrium mixture, the concentration of titratable iodine increased. The photochemical reaction was believed to be a reduction of ferricyanide to ferrocyanide by iodide, the absorption being almost entirely by the tri-iodide ion. One molecule of iodine was formed for each quantum absorbed. In discussing the possible mechanism of the reaction, these authors suggested the possibility that an iodine atom might react with an iodide ion to produce the ion I_2^- which might then serve as the reducing agent for the ferricyanide.

It is the opinion of Schwarz and Tede[208] that potassium ferricyanide is not appreciably sensitive to light, decomposition taking place to a very slight extent after intense illumination. The change consists in hydrolysis to aquo-complex salts and ultimately ferric hydroxide, and also in the oxidation of hydrocyanic acid to cyanogen with the production of potassium ferrocyanide. In the case of potassium cobalticyanide, the reaction is

$$K_3Co(CN)_6 + H_2O \longrightarrow K_3Co(CN)_5OH + HCN$$

and

$$K_3Co(CN)_6 + H_2O \longrightarrow KCN + K_2Co(CN)_5H_2O.$$

The corresponding chromium compound behaves similarly to the cobalticyanide, but the manganese compound is rapidly decomposed in the absence of light into manganic hydroxide, hydrocyanic acid and potassium cyanide.[209]

Pavolini[210] observed that when paper is coated with a solution of 5-per cent potassium ferricyanide and 5-per cent ammonium molybdate, a print can be made on exposure to sunlight. The exposed print can be fixed in water acidulated with 1-per cent hydrochloric acid. If, on the other hand, these compounds are added to a gelatin or gum arabic solution, the gelatin is rendered insoluble by the decomposition products formed on exposure to light. This mixture produces the same result as do dichromates.

A weak source of light is capable of increasing by about 10 per cent the rate of oxidation of hydrazine by the ferricyanide ion. The effective rays are those absorbed by the ferricyanide.[211]

An aqueous solution of sodium nitroprusside when exposed to sunlight in an open vessel is decomposed into hydrogen cyanide, sodium nitrite and $Na_2Fe_2(CN)_6$, the latter, in the presence of sodium hydroxide, being converted into Prussian blue.[212] If the exposure to sunlight takes place in a closed vessel, nitric oxide is evolved.

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[207] Dickinson, R. G., and Ravitz, S. F., *J. Am. Chem. Soc.*, **52**, 4770 (1930).

[208] Schwarz, R., and Tede, K., *Ber.*, **60**, 69 (1927).

[209] For observations on sodium nitroferrocyanide, see Justin-Mueller, E., *Bull. soc. chim.*, **2**, 1932 (1935).

[210] Pavolini, T., *Corr. fot.*, **26**, 723 (1929); *Chem. Abs.*, **24**, 2958 (1930).

[211] Gilbert, E. C., *J. Phys. Chem.*, **35**, 3631 (1931).

The precipitates formed on mixing a concentrated aqueous solution of sodium nitroprusside with aqueous solutions of silver nitrate, mercuric nitrate, or ferrous sulfate, suffer change after exposure to sunlight for ten minutes.[213]

Potassium permanganate and potassium dichromate are very stable towards ultraviolet light.[214]

Although the chromates of ammonium, potassium and sodium are unaffected by sunlight in the absence of substances capable of oxidation, in the presence of such substances the photochemical reduction of the chromates and dichromates occurs rapidly under the radiations of an arc light.[215] The reduction results in either a brownish precipitate or a green solution according to the properties of the substance which serves as reducing agent. In some cases there is an evolution of gas, either ammonia, in the case of ammonium chromates, or carbon dioxide. According to Bhattacharya and Dhar,[216] the orders of the reactions between chromic acid and the following acids in sunlight and in darkness are, respectively: citric acid, 2, 2.5; tartaric acid, 2,3; lactic acid, 3, 3. Manganous sulfate accelerates most of the reactions and, except in the case of tartaric acid, reduces the order. With decrease in the order of the reaction, the temperature coefficients of the velocity coefficients usually rise. The temperature coefficient for the photochemical reaction is always greater than unity but less than that of the dark reaction with the same acid. In all cases, several molecules react for each quantum absorbed, the number increasing with increase in the concentration and with the temperature. The rate of reaction with or without manganous sulfate is directly proportional to the intensity of the incident radiation, except in the reactions with citric and tartaric acids in the absence of manganous sulfate, the rates of which are proportional to the square root of the intensity of the radiation.

Forbes and Leighton[217] electrolyzed 0.006 to $0.05N$ chromate solutions in normal and three normal sulfuric acid between platinum electrodes at various current densities, comparing the yields obtained in the light of a 1500-watt quartz mercury arc and in darkness. At an illuminated cathode, a 0.5 per cent greater efficiency was observed. Part or all of the increased efficiency could be attributed to local heating in a thin diffusion layer at the cathode. An absence of any increase in yield in light would be compatible with the existence of light-sensitive chromate if the latter is equally reactive electrochemically before and after photoexcitation. Granting, however, that the slightly greater electrochemical efficiency in light may be due in part to excited chromate, it would be impossible to estimate the quantum yield without making certain assumptions, especially one regarding the life of the excited molecule, upon which would depend its chance of reaching the cathode.

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[212] Justin-Mueller, E., *Bull. soc. chem.*, **2**, 1932 (1935).

[213] Leffmann, H., and Pines, C. C., *Bull. Wagner Free Inst.*, **4**, 41 (1929); *Brit. Chem. Abs*, **A**, 1431 (1929).

[214] Mathews, J. H., and Dewey, L. H., *8th Intern. Congr. Appl. Chem Sect. IX, Orig. Comm.*, **20**, 247 (1912). For data on the absorption of chromic acid, potassium chromate and dichromate and permanganate solutions, see Viterbi, E., and Krausz, G., *Gazz. chim. ital.*, **57**, 690 (1927); Bhagwat, W. V., and Dhar, N. R., *J. Indian Chem. Soc.*, **7**, 913 (1930); *Chem. Abs*, **25**, 2053 (1931); Tawde, N. R., *J. Indian Chem. Soc*, **8**, 499 (1931); *Chem Abs*, **26**, 395 (1932); Rao, A. L. S., *Current Sci.*, **6**, 154 (1937); *Brit. Chem. Abs.*, **AI**, 59 (1938); *Proc. Indian Acad. Sci*, **6A**, 293 (1937).

[215] Plotnikow, J., *Bull. acad. sci. Russ.*, 1093 (**1919**); *Chem. Abs.*, **17**, 2231 (1923).

[216] Bhattacharya, A. K., and Dhar, N. R., *Z. anorg. Chem.*, **169**, 381 (1928); see also Wulff, P., and Ammann, H., *Compt. rend. IX, Congr. int. Phot. Sci. appl.*, 10 pp., 1935; *Brit. Chem. Abs.*, **AI**, 90, 1938; Ammann-Brass, H., *Z. wiss. Phot.*, **36**, 33 (1937); *Brit. Chem. Abs.*, **A**, 255, 1937. For the use of a formic acid-formate buffer in the photoreduction, see Wulff, P., and Ammann, H., *Compt. rend., IXe int. Photo. sci. appl.*, **1935**; *Chem. Abs.*, **31**, 8381 (1937).

[217] Forbes, G. S., and Leighton, P. A., *J. Phys. Chem.*, **30**, 1628 (1926).

Morton[218] finds that, under suitable conditions, as in the presence of ethyl alcohol, dichromate solutions are affected by light absorbed by the dichromate. With increasing acidity, the oxidizing power of the dichromate solutions in darkness increases so that the apparent action of light decreases.

Reactions between potassium dichromate and gelatin under the influence of light have been studied and have been applied in photography. The photochemical mechanism is not yet understood, and no attempt will be made to review the early work on the nature of the reaction. According to Plotnikow and Karschulin,[219] the reaction begins at 5950A, reaches a maximum at 5000A and then decreases to about 2400A, at least in the case of films sensitized with potassium dichromate and cresyl blue, 2BS. On the other hand, Eder[220] found the action of light on chromated gelatin to begin at 550mμ, to reach a maximum between 470 and 430mμ, and to become very slight beyond 380mμ.[221] Popovitzkiĭ[222] states that from earlier work of Eder, it is known that gelatin so transformed represents a compound with chromium salts, no organic oxidation products entering the composition. Popovitzkiĭ suggested the formula $4Cr_2O_3 \cdot 3CrO$, for the chromium complex, which agreed better with the analytical results than the formulas $Cr_2O_3 \cdot 2CrO_3$ or $Cr_2O_3 \cdot 3CrO_3$ suggested by Eder and Lumière Brothers and Seyewetz. In order to employ the Werner coördination number of six for chromium compounds, the formula given above should be doubled. Two photochemical reactions might be written to account for its formation:

$$16K_2CrO_4 . CrO_3 \longrightarrow 16K_2CrO_4 + 8Cr_2O_3 + 12O_2.$$
$$6K_2CrO_4 . CrO_3 \longrightarrow 6K_2CrO_4 + 6CrO_3.$$

It is presumed that the gelatin having absorbed but not combined with the liberated oxygen can enter into combination with the 8 Cr_2O_3 and 6 CrO_3 with greater ease. Galinsky[223] suggests that the change resembles a protein denaturation, although no change in the Hausmann numbers or in the digestibility was detected.

The decomposition of chromyl chloride by light into CrO_2 and chlorine, from the nature of the absorption spectrum, requires wave-lengths shorter than 4200A.[224]

Tin Compounds. The molecular absorption coefficient of a solution containing 32.7 gm. stannous chloride per liter and 0.811*N* in hydrochloric acid corresponds to complete absorption for wave-lengths shorter than 2850A, partial absorption from 3020 to 3340A and complete transmission of wave-lengths longer than 3650A. Stannous chloride solutions do not follow Beer's law, probably because of the formation of such absorbing complexes as $HSnCl_3$ and H_2SnCl_4 in the presence of increasing amounts of acid. Quantum yield determinations indicate the photochemical oxidation of such solutions to be a chain reaction. Both the photochemical and the thermal reactions are similarly affected by accelerators and inhibitors so that the same chain mechanism probably applies to both.[225]

In benzene solutions, the absorption spectra of stannic iodide exhibit maxima which indicate a dissociation yielding an unexcited iodine atom at 3650A and an excited one at 2850A. In ethyl alcohol, the latter dissociation occurs at 2950A. In methyl alcohol, no maxima are evident.[226]

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[218] Morton, D. S., *J. Phys. Chem*., **33,** 1135 (1929).

[219] Plotnikow, J., and Karschulin, M., *Z. Physik,* **26,** 277 (1926).

[220] Eder, J. M., *Z. Physik,* **37,** 235 (1926).

[221] For a general discussion, see Schömmer, F., *Phot. Rundschau,* **63,** 120, 138 (1926); Elòd, E., and Berczeli, H., *Kolloid-Z.*, **74,** 305 (1936).

[222] Popovitzkiĭ, A., *J. Russ. Phys. Chem. Soc.*, **55,** 1 (1924); *Chem. Abs.*, **19,** 1664 (1925).

[223] Galinsky, A., *Biochem. J.*, **24,** 1706 (1930).

[224] Kantzer, M., *Bull. soc. franc. phot.*, **20,** 167 (1933); *Chem. Abs.*, **28,** 4982 (1934); *Compt. rend.*, **196,** 1882; **198,** 1226 (1934); **201,** 1030 (1935).

[225] Haring, R. C., and Walton, J. H., *J. Phys. Chem.*, **37,** 375 (1933).

Certain stannic acids produced either as a result of changes occurring in gelatinous orthostannic acid or formed by the action of nitric acid on tin, acquire a blue coloration on exposure to the ultraviolet rays of sunlight in the presence of certain organic reducing agents, as tartaric, citric and oxalic acids or ethanol. This action is irreversible and is accompanied by decomposition of the reducing agent without visible evolution of gas. The blue color is stable and permanent in the absence of air. The latter destroys the color. Under the same conditions, orthostannic acid does not give the coloration.[227]

According to Harada,[228] the formation of the substance $((CH_3)_3Sn)_2O \cdot (CH_3)_3SnI \cdot H_2O$, by the action of sunlight on tin trimethyl iodide (trimethyliodostannane), does not take place unless tin tetramethyl is present.

Mercury and Its Compounds. About 1924-5, Miethe[229] and Stammreich[230] claimed to effect the transformation of mercury into gold by the use of a new type of mercury vapor arc with very high energy input. Nagaoka, of Tokyo,[231] independently made similar claims, which for a time were accepted by Haber. Miethe believed he had obtained one part of gold from 100,000,000 parts of mercury, and Nagaoka, by passing high tension sparks between pure tungsten points and mercury under paraffin, claimed to have increased the yield ten thousand times. A sample of gold prepared by the latter is said to have been placed in the American Museum of Natural History.[232] Hönigschmid and Zintl[233] reported Miethe's material to have an atomic weight of 197.26. The claims called forth a number of papers,[234] some of which contained further confirmatory claims and others of which speculated as to the nature of the intranuclear transformations. The Siemens Works attempted the bombardment of mercury surfaces by electrons in high vacuum, and even patented certain processes for effecting the transformation.[235]

Doubts were soon raised on many sides. Tiede, Schleede and Goldschmidt,[236] found that mercury purified by two vacuum distillations was free of gold and gave no gold by Miethe's process and Aston[237] rejected the claims on theoretical grounds. Many workers subsequently reported failures in attempts to duplicate these experiments.[238] Further discussion of reported transmutations of metals by ultraviolet radiations is unnecessary, since the energies required are greater than are available from the usual sources of ultraviolet.

Ether solutions of mercuric chloride (10 gm.) after exposure to sunlight in sealed bottles for a period of five months formed 3.2 gm. of calomel containing an organic substance; the ether contained hydrogen chloride, aldehydes and chlorinated compounds.[239] Pougnet[240] exposed a solution of mercuric chloride in a quartz tube to a mercury vapor lamp. He found that the tube became cloudy almost immediately because of the formation of calomel. After thirty minutes, 42 per cent had been decomposed and the calomel began to darken. After seventy minutes, when the decomposition reached 48 per cent, the reaction ceased, indicating the reaction to be reversible.

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[227] Billen, F., *Ingenieur chimiste*, **9**, 60 (1925); *Chem Abs*, **21**, 1933 (1927).

[228] Harada, T., *Bull. Chem. Soc. Japan*, **2**, 105 (1927).

[229] Miethe, A., *Naturwiss.*, **12**, 597 (1924); *Chem Abs.*, **18**, 3139 (1924); *Naturwiss.*, **13**, 635 (1925)

[230] Stammreich, H., *Z. anorg allgem. Chem*, **148**, 93 (1925); **150**, 350, **158**, 185 (1926).

[231] Nagaoka, H., *Ind Eng. Chem, News Ed.*, **3**, 1 (1925); *Naturwiss*, **13**, 682 (1925)

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[233] Hönigschmid, O., and Zintl, E., *Naturwiss.*, **13**, 644 (1925).

[234] Retschinsky, T., *Physik. Z.*, **26**, 280 (1925); Bernhardt, F., *Physik. Z*, **27**, 713 (1926); Gaschler, A., *Z. Elektrochem*, **32**, 186 (1926); Kaul, L., *Metallbörse*, **14**, 1432; von Antropoff, A, *Z. angew Chem.*, **37**, 827 (1924).

[235] French P. 598,140 (1925), to Siemens-Werke A.-G.; British P. 243,670, 1925, 247,508, 1925, and 248,318, 1925.

[236] Tiede, E., Schleede, A., and Goldschmidt, F., *Ber.* **59**, 1629 (1926); Riesenfeld, E, and Haase, W., *Ber.*, **58**, 2828 (1925); Miethe, A., and Stammreich, H., *Ber.*, **59B**, 359 (1926).

[237] Aston, F. W., *Nature*, Dec. 19, 1925; Riesenfeld, E., and Haase, W., *Ber*, **59**, 1625 (1926).

[238] Piutti, A., and Boggio-Lera, E., *Giorn. chim. ind. applicata*, **8**, 59 (1925); Garrett, M. W., *Nature*, **118**, 84 (1926); *Proc. Roy. Soc.*, **112A**, 391 (1926); Shelton, H., and Estey, R, *Phys. Rev.*, **27**, 515 (1926); *J. Frank. Inst.*, July 22, **1926**; Harkins, W. D., *Science*, **63**, 1636 (1926); Duhme, E., and Lotz, A., *Ber.*, **59**, 1649 (1926); Haber, F., Jaenicke, J., and Matthias, F., *Ber*, **59**, 1641 (1926); *Z. anorg. Chem*, **153**, 153 (1926); Wolfers, F., *J. chim. phys.*, **24**, 727 (1927).

In solutions of mercuric chloride of relatively low concentration the photochemical reduction by ferrous chloride goes at a rate nearly independent of the concentration of the ferrous salt.[241] For a given concentration of the latter, the rate increases at first with the amount of mercuric chloride and then diminishes. The maximum rate appears to be attained when the salts are present in equimolar quantities (3 molar). Under these conditions, oxygen does not affect the reaction, but when there is a large excess of ferrous chloride, it reduces the quantity of calomel obtainable. The most effective wave-lengths appeared to be shorter than 2650A.

When an alcoholic solution of hydrogen sulfide is gradually added to mercury halides in suspension or in solution, complex compounds of the general formula $HgX_2 \cdot 2HgS$ result. These compounds, of various shades of red and yellow, readily undergo a color change in direct or diffuse daylight, regaining their original colors in darkness.[242]

Mercuric iodide, in solutions less than 1.5 molar in potassium hydroxide, is converted into the unstable dark red $HgI_2 \cdot HgO$, which decomposes into mercuric oxide, but is unaffected by light.[243] In more alkaline solutions (2-6 molar), there is formed a white complex, $3HgI_2 \cdot HgO \cdot 3KOH$, which is decomposed into HgO by light. In solutions stronger in alkali than 7 molar, there is formed a white complex, $HgI_2 \cdot 2(\text{or } 3)HgO \cdot XKOH$ which, when dried, is slowly decomposed by light.

Lüppo-Cramer[244] finds that red mercuric iodide present with gum arabic in a gelatin film is light- and color-sensitive, forming a developable latent image.

Cinnabar is blackened by ultraviolet light,[245] but the nature of the reaction has not yet been explained. Cropp[246] attributed it to a decomposition into the elements.

Mercurous sulfate also darkens rapidly and independently of the presence of air. Skinner[247] does not believe there to be production of mercury and mercuric salt and suggests that a dark subsalt or a polymeric modification may be formed.

Halogen mercury thiocyanates are phototropic, and complex halides of mercury such as HgIBr, HgICl and HgBrCl, are somewhat less so.[248]

Cobalt and Nickel. The differences in color of aqueous cobalt salts under various conditions have been the subject of a great number of investigations, but these lie beyond the scope of the present text.[249]

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[239] Puxeddu, E., *Gazz. chim. ital.*, **59**, 160 (1929).

[240] Pougnet, J., *Compt. rend.*, **161**, 348 (1915); *J. Soc. Chem. Ind.*, **34**, 1053 (1915).

[241] Winther, C., *Z. wiss. Phot.*, **11**, 60 (1912); *Chem. Abs.*, **6**, 2042 (1912).

[242] Varalalu, T., Ram, A., and Rao, B., *J. Sci. Assoc. Maharajah's College, Visianagaram*, **1**, 107 (1924); *Chem. Abs.*, **18**, 3529 (1924).

[243] Montignie, E., *Bull. soc. Chim.*, **2**, 290 (1935); *Brit. Chem. Abs.*, **A**, 458 (1935).

[244] Lüppo-Cramer, *Phot. Korr.*, **65**, 97 (1929); *Chem. Abs.*, **25**, 885 (1931).

[245] Brosset, C., *Naturwissen.*, **24**, 813 (1936).

[246] Cropp, W., *Proc. Austral. Inst. Met.*, No. **52**, 259 (1923).

[247] Skinner, S., *Proc. Cambr. Phil. Soc.*, **12**, 260 (1904); *J. Chem. Soc.*, **86**, ii, 173 (1904).

[248] For further discussions of phototropy in other complex mercury compounds, see Rao, S. V. R., and Watson, H. E., *J. Phys. Chem.*, **32**, 1354 (1928), and Rao, E. L., Varahalu, K., and Narasimhaswami, M. V., *Nature*, **124**, 303 (1929). Slight decomposition is believed to account for the yellow to brown color formed on the irradiation of mercury fulminate by A. Borocco, *Compt. rend.*, **207**, 166 (1938).

Baly [250] finds that on exposure to daylight in the air, nickel carbonate reversibly darkens in color, due to the production of Ni_2O_3 or nickel hydroxide. Extraction of the blackened material with warm water yielded a small amount of formaldehyde, and on evaporation of the filtrate, it was claimed that there were found the nickel salts of some organic acids and some carbohydrate. Similar results were obtained also, it was claimed, with cobalt carbonate.

Cobalt trinitrotriammine in acid solution decomposes completely to cobaltous salts both in light and in darkness. In the dark reaction, there are two stages, each being a unimolecular process. The intermediate product is light-sensitive, radiations of 3660A causing decomposition with a quantum yield of 0.37.[251] On the other hand, the photodecomposition of the cobalt trinitrotriammine appeared to take place in one stage, the velocity, unlike that of the dark reaction, being independent of the acid concentration. The quantum yield is 0.2 (3660A) and the temperature coefficient 1.03 for the velocity.

On illumination of a solution of racemic $K_3Co(C_2O_4)_3$ by dextrocircularly polarized light (5890A), the cobalt compound becomes levorotatory.[252] The decomposition of this compound (0.02-0.002M) by 4360, 4050, 3660 and 3130A is a reaction of zero order, according to Murgulescu,[253] who formulates it

$$\mathrm{Co(C_2O_4)_3} + h\nu \longrightarrow \mathrm{CO(C_2O_4)_2} + \mathrm{(C_2O_4)'}$$
$$\mathrm{Co(C_2O_4)_3'''} + \mathrm{(C_2O_4)'} \longrightarrow \mathrm{(C_2O_4)''} + 2\mathrm{CO_2} + \mathrm{Co(C_2O_4)_2''}$$

in agreement with Jäger and Berger, but not with Vranek.[254]

The hydrolysis of aqueous solutions of hexamminecobaltic chloride, nitroamminecobaltic chloride, *cis* and *trans*-dinitrotetrammine cobalt, the two forms of trinitrotriamminecobalt, and *cis*-tetranitrodiamminecobalt are greatly accelerated by light.[255] The cobalt separates, except from dilute solutions in which it remains as sol, as brownish-black cobaltic hydroxide, nitrite ions remaining in the solutions. The photochemical decomposition of all these nitritoamminecobalt compounds is an irreversible reaction of the first order in which the wave-length 3660A is most active. Increase in the number of nitro-groups in the nucleus diminishes the photochemical stability; trinitrotriamminecobalt occupies an intermediate position because of its electrically neutral nucleus. Among stereoisomeric salts, the *trans* compound is the more stable. The velocity of reaction is about one and one-half times as great in acid as in neutral solutions, but is largely independent of the pH. According to Schwarz and Tede,[256] the stability of the complex nucleus diminishes with increasing electroaffinity of the coördinately united anion, in the decreasing order, carbonate, oxalate, nitrite, bromide, chloride, sulfate. The inverted position of the oxalate and nitrite ions is attributed to stereochemical factors and probable ring formation in the case of the oxalato-residue. In the cobaltpentammine series, the sequence is carbonate, chloride, oxalate, sulfite, nitrite, nitrate (equal to sulfate). The exceptional position of the chloride ion is due to its non-complex character. The presence of water molecules in the complex increases the tendency to hydrolyze. The complex compounds of chromium are less stable and more subject to photochemical change than are those of cobalt.

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[249] Mazetti, C., *Gazz. chim. ital.*, **56**, 589, 595 (1926), Hantzsch, A., *Z. anorg. Chem.*, **159**, 273 (1927); Vaillant, P., *Compt. rend.*, **189**, 747 (1929); Brode, W R., *Proc. Roy. Soc*, **118A**, 286 (1928); Brode, W. R., and Morton, R. A., *ibid.*, **120A**, 21 (1928); Brdicka, R., *Collection Czechoslov. Chem. Comm.*, **2**, 545 (1930); *Chem. Abs.*, **25**, 467 (1931); Howell, O. R., and Jackson, A, *Proc. Roy. Soc.*, **142A**, 587 (1933); Macwalter, R. J., and Barratt, S., *J. Chem. Soc.*, 517 (**1934**).

[250] Baly, E. C. C., *Phot. J.*, **72**, 474 (1932).

[251] Luther, R., and Frieser, H., *Z. Elektrochem.*, **36**, 141 (1930).

[252] Tsuchida, R., Nakamura, A., and Kobayashi, M., *J. Chem. Soc Japan*, **56**, 1335 (1935); *Brit. Chem. Abs.*, **AI**, 318 (1937).

[253] Murgulescu, I. G., *Bul. soc. stiinte Cluj*, **8**, 193 (1935); *Chem. Abs.*, **30**, 4402 (1936).

[254] Vranek, J., *Z. Elektrochem.*, **23**, 340 (1917).

[255] Schwarz, R., and Weiss, H., *Ber.*, **58**, 746 (1925).

[256] Schwarz, R., and Tede, K., *Ber.*, **60**, 63 (1927).

Tungsten and Molybdenum. The light-sensitivity of the reduction of tungstic acid by glucose to a blue product was studied by Vasilief-Sinzova.[257] The reduction appeared to follow a monomolecular course. The light-sensitivity of freshly prepared solutions of tungstic acid increases with increase of the concentration of added hydrochloric acid up to 0.47 normal, and then decreases, perhaps because the number of molecules of H_2WO_4 sensitive to light increases until the coagulating effect of the acid predominates.

Underlying these observations is the fact that when aqueous solutions of alkali tungstates are gradually acidified, amorphous precipitates of hydrated forms of tungsten trioxide are finally obtained. Before the precipitate is actually formed, polymerization changes occur in the dissolved tungstic acid, hexatungstic acid being first produced. With the addition of more acid there is a further polymerization to metatungstic acid, which is probably a diparatungstic acid, and in the presence of other acids, such as arsenic and phosphoric, heteropolytungstic acids are formed. These changes have been followed by light absorption and diffusion methods.[258] Such reactions have been made the basis of a patent for ultraviolet-sensitive layers suitable for actinometric purposes.[259] The layer contains compounds of molybdenum, tungsten or thallium, together with an oxidizable substance as glucose, made slightly acid by hydrochloric or citric acids. On exposure to wave-lengths shorter than 4000A, the layer changes from white to blue.

Hanzawa[260] described a chemical actinometer using ammonium molybdate in dilute hydrochloric acid containing small quantities of ethanol. Ghosh and Bhattacharya[261] find the photochemical reduction of tungstic and molybdic acid sols by alcohol to be of zero order. The velocity constants were found to decrease in sols which had aged, but the velocity constants of the latter could be increased to values greater than those of fresh sols by heating at 70°C. for eight minutes. In the presence of univalent ions the sols are less light sensitive. According to Sachs,[262] the best method for the preparation of molybdenum blue is the reduction of a solution of sodium molybdate, acidified with hydrochloric acid, by formic acid in the light of a mercury arc. Hydrogen may also serve as the reducing agent.[263]

When exposed to sunlight in a sealed bottle, an ether solution of titanium tetrachloride turned brown during the second day, and ultimately became green. On low temperature evaporation of the solvent, the mixture became violet, suggesting the green and violet modifications of titanium trichloride.

The Rare Earths. Boll[264] studied the rate of hydrolysis of tetrachloroplatinic acid when submitted to radiations of different energy, the amount of radiation reaching the solution being controlled by a cell containing a dilute solution of caffeine, the concentration and thickness of the caffeine layer being varied. A later study by Boll[265] of the reaction in very dilute aqueous solution shows the progress of the photochemical reaction by measuring the increase in the electrical conductivity of the solution.

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[257] Vasilief-Sinzova, A., *J. Chim. Ukraine*, **1**, 425 (1925); *Chem Abs.*, **20**, 2792 (1926).

[258] Jander, G., Majert, D., and Aden, T., *Z. anorg. Chem.*, **180**, 129 (1929).

[259] Sheppard, S E., and Eberlin, L. W., U. S. P. 1,934,451, Sept. 11, 1933, to Eastman Kodak Co.; *Brit Chem. Abs.*, **B**, 873 (1934).

[260] Hanzawa, T., *J Agr. Chem. Soc. Japan*, **6**, 1093 (1930); *Chem. Abs.*, **25**, 2643 (1931).

[261] Ghosh, S., and Bhattacharya, A. K, *J. Indian Chem. Soc.*, **7**, 717 (1930); *Chem. Abs.*, **25**, 252 (1931); *Bull. Acad. Sci. United Provinces Agra Oudh, India*, **2**, 29 (1932); *Chem. Abs.*, **27**, 2097 (1933).

[262] Sachs, D., *J. chim phys.*, **29**, 474 (1932).

[263] Krauss, F., and Bruchhaus, E., *Z. anorg. allgem. Chem*, **189**, 53 (1930).

[264] Boll, M., *Compt. rend.*, **156**, 138 (1914); *J. Chem. Soc.*, **104**, ii, 171 (1913). For data on various platinum complexes, see Lifschitz, I., and Froentjes, W., *Z. anorg. allgem. Chem.*, **233**, 1 (1937).

By the action of hydrogen and short ultraviolet rays, Krauss and Bruchhaus[266] reduced a brown solution made by dissolving ruthenium hydroxide in hydrochloric acid to a bright, transparent, orange-colored solution, containing bivalent ruthenium. Colorless liquid ruthenium pentacarbonyl in light evolves carbon monoxide and produces orange-red, pseudo-hexagonal plates of $Ru_2(CO)_9$. The latter, when dissolved in glacial acetic acid become lilac in sunlight.[267]

Ultraviolet light causes the liberation of oxygen from a 0.1 molar solution of ceric perchlorate in molar perchloric acid. The quantum efficiency is at first about 0.1. Since the perchlorate ion is not decomposed, the following mechanism was suggested by Weiss and Porret.[268]

$$\begin{aligned}
&Ce^{++++} + h\nu \longrightarrow Ce^{++++} \text{ (excited).}\\
&Ce^{++++} \text{ (excited)} + H_2O \longrightarrow Ce^{+++} + H^+ + OH\\
&OH + OH \longrightarrow H_2O + O\\
&O + O \longrightarrow O_2.
\end{aligned}$$

The accumulation of Ce^{+++} retards the reaction, probably by the loss of an electron to the OH molecule with formation of Ce^{++++} and the hydroxyl ion.

Uranium Compounds. Uranium is the only element other than the rare earths, whose compounds exhibit line absorption spectra.[269]

An acid mixture of solutions of sodium hypophosphite and uranyl sulfate remains unchanged in darkness, but when exposed to light, rapidly deposits a green colloidal precipitate containing 54.5-56 per cent of uranium and 15.75-17.5 per cent of phosphorus, and consisting of hypophosphite with some phosphite and phosphate, mixed with sodium phosphate and uranous sulfate.[270]

Frequent examples of the use of uranyl salts as photosensitizers will be found in other chapters, particularly in connection with the photochemical behavior of the organic acids. Rousseau[271] subjected salts or solutions of salts of uranium, manganese, iron or nickel to the action of solar or ultraviolet radiation, and then added the irradiated salts to liquids in which photocatalysis or the sterilization or activation of ferments is to be effected.

Zinc oxide has also been widely employed as a photosensitizer. Winther[272] found that when certain samples of zinc oxide were strongly illuminated, in the presence of air, by light filtered through ordinary glass, a substance appeared in the gas phase which was capable of oxidizing iodide ion to iodine. In the use of this zinc compound for photosensitization of the decomposition of silver salts to sunlight

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[265] Boll, M., *Ann. Phys*, **2,** 54, 266 (1914); *J. Chem Soc.*, **108,** ii, 123 (1915).

[266] Krauss, F., and Bruchhaus, E., *Z. anorg allgem. Chem*, **189,** 53 (1930).

[267] Manchot, W., and Manchot, W. J., *Z. anorg. allgem. Chem*, **226,** 385 (1936).

[268] Weiss, J., and Porret, D., *Nature*, **139,** 1019 (1937).

[269] Details of the absorption and fluorescence spectra of uranium compounds are given by van Heel, A., *Comm. Phys. Lab. Univ. Leiden, Suppl. No* **55B** to *Nos.* **169–180** (1925), *Chem Abs*, **21,** 3311 (1927); Ephraim, F., and Mezener, M., *Helv. Chim. Acta*, **16,** 1257 (1933); Ghosh, J C, and Mittra, B. N., *Quart. J. Indian Chem. Soc*, **4,** 353 (1928); Levshin, V. L., *Bull acad. sci., U.R S.S, Classe sci. math. nat., Ser. Phys.*, **No. 2,** 185 (1937); *Chem. Abs.*, **31,** 8380 (1937) For the photochemical liberation of iodine from potassium iodide by uranyl sulfate solutions, see Montignie, E, *Bull soc. chim.*, **5,** 564 (1938).

[270] Dienert, F., and Villemaine, F., *Compt. rend.*, **199,** 1113 (1934). See also Chretien, A, and Kraft, J., *Compt. rend.*, **204,** 1736 (1937).

[271] Rousseau, E., British P. 226,534, Dec. 13, 1924; *Brit. Chem. Abs.* **B,** 406 (1926).

[272] Winther, C., *Z. wiss. Phot.*, **21,** 168 (1921).

$$2AgNO_3 + ZnO \longrightarrow 2Ag + Zn(NO_3)_2 + 1/2O_2,$$

Perret[273] found silver peroxide to be formed as an intermediary product. In the reduction of mercuric chloride to calomel by zinc oxide in sunlight, four to fifteen days were required for a notable transformation; the reaction attained a stationary state. When the reaction is of zero order, it is greatly accelerated by dextrose and by sucrose. In the presence of air, the sensitizing action of zinc oxide on the photolysis of calomel consists in the simultaneous oxidation and reduction of the salt. Bhattacharya and Dhar[274] listed twenty-nine reactions sensitized by zinc oxide, including among others, the separation of gold from its chloride, the oxidation of potassium iodide by potassium persulfate, oxidation of sodium nitrite by iodine, oxidation of hydroxylamine or of hydrazine by iodine, decomposition of mercuric oxide, and decomposition of aqueous solutions of potassium permanganate or of potassium persulfate.

To account for the inactivity of many samples of zinc oxide, Jung and Kunau[275] studied samples prepared by various methods. Only those obtained by roasting the nitrate proved to be active which suggested that a zinc oxynitrate rather than the oxide might be the true photosensitizing agent. McMorris and Dickinson[276] identified nitrogen dioxide as the gaseous product formed in small quantity when zinc oxide (prepared from the nitrate) is strongly illuminated, in a stream of oxygen, by the mercury arc radiations filtered through water and Pyrex glass. Baur[277] held that on the absorption of energy, zinc oxide is converted into a "phototrope," one-half of which is capable of oxidizing a neighboring substance, while the other half reduces the same substance. Such a conception of intramolecular electrolysis is however, unnecessary for the explanation of photosensitization by zinc oxide, since it has been found that a gaseous oxidizing agent is liberated from zinc oxide on irradiation.

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[273] Perret, A., *J. chim. phys.*, **23**, 97 (1926).

[274] Bhattacharya, A. K., and Dhar, N. R., *Quart. J. Indian Chem. Soc.*, **4**, 299 (1927), *Chem. Abs.*, **22**, 915 (1928).

[275] Jung, G., and Kunau, E., *Z. physik. Chem.*, **15B**, 45 (1931).

[276] McMorris, J., and Dickinson, R. G., *J. Am. Chem. Soc.*, **54**, 4248 (1932)

[277] Baur, E., *Trans. Faraday Soc.*, **21**, 627 (1925), see also Chapter 16.

Chapter 21

Photochemical Reactions of Inorganic Solids

The present theories of photoprocesses in crystals have resulted from attempts to interpret the experimental studies of the effects of the absorption of light by ionic alkali halide crystals by the methods of quantum mechanics recently developed for the study of the properties of metals.[1] In large part, the experimental foundation has been laid at Göttingen, as an extension of the studies of Gudden and Pohl[2] on the photoconductivity of certain homopolar crystal lattices, notably the diamond. After a number of attempts had been made to obtain similar measurements upon variously colored rock salt crystals,[3] a thorough study was undertaken of the formation by ultraviolet light of a yellow color in alkali halides. This phenomenon had been observed by Goldstein[4] as early as 1896. To obtain an understanding of the nature of this process, Hilsch and Pohl[5] made observations of the far ultraviolet (including the Schumann region) absorption spectra of a number of alkali halides. In some cases, the halides were deposited upon quartz plates by vacuum sublimation. It was found that the nature of the absorption was determined primarily by the halogen ions, and was relatively but little influenced by the nature of the cation. The extinction curves showed definite sharp maxima. Absorption in these bands was believed to effect a transfer of an electron from a halogen ion of the crystal lattice to an adjacent metal cation, producing free halogen and metal atoms. In each case, the band of longest wave-length (corresponding to the absorption of the smallest effective quantum) was attributed to the liberation of the atoms in their normal states. The energy required for this was at first held to be equal to, first, that required to separate an electron from a halogen ion (its electron affinity E) and, second, that required to overcome the coulombic attraction between the sodium and halogen ions (the coulombic part of the lattice energy of the crystal Q). This energy requirement would be diminished by the work necessary to ionize the alkali atom (its ionization potential I), since this energy is liberated when the ion is converted into the atom. From available data, the values of $Q+E-I$ were calculated for the various halides studied. The correspondence between the calculated energy values and the energy corresponding to the first absorption maxima was only fairly satisfactory. The value calculated for the mean of the lithium, sodium, potassium and caesium iodides was 5.76 electron-volts and the observed value was 5.56 electron-volts.[6, 7]

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[1] Bloch, F., *Z. Physik,* **52,** 555 (1928); **59,** 208 (1930); Wilson, A. H., *Proc Roy. Soc. London,* **133A,** 458 (1931); **134A,** 277 (1931), Peierls, R., *Ann. Physik,* **4,** 121 (1930).

[2] Gudden, B., and Pohl, R., *Z. Physik,* **16,** 170 (1923); **17,** 331 (1923).

[3] Gyulai, Z., *Z. Physik,* **32,** 103 (1925); **35,** 411 (1926); Flechsig, W., *Ibid*, **46,** 788 (1928).

[4] Goldstein, E., *Z. Instrdkc,* **16,** 211 (1896).

[5] Hilsch, R., and Pohl, R. W., *Z. Physik,* **57,** 145 (1929); **59,** 812 (1929); **64,** 606 (1930); **68,** 721 (1931). For earlier observations, see Pfund, A. H., *Phys. Rev.*, **32,** 39 (1928) and for other halides, Ottmer, R., *Z. Physik,* **46,** 798 (1928).

[6] See also Bonhoeffer, K., and Harteck, P., "Grundlagen der Photochemie," p. 141, Dresden, T. Steinkopff; Sponer, H., "Molekülspektren und Ihre Anwendung auf Chemisch Probleme," II, 339-361, Berlin, J. Springer. de Boer, J. H., "Electron Emission and Adsorption Phenomena," Cambridge Univ. Press, 1935, 239.

The absorption maxima at shorter wave-lengths were attributed to the liberation of the elements in excited states. The difference between the first and second maxima in the spectra of the iodides of alkalies other than caesium, expressed in volts, was 1.02. That between the $^2P_{3/2}$ and $^2P_{1/2}$ states of the iodine atom, is, from atomic spectra, 0.937 volt. In the case of the bromides, the corresponding values were 0.52 volt from the separation of the absorption maxima of the crystals and 0.454 volt from atomic spectra.

The third maximum observed in the iodide spectra was attributed to the production of a normal halogen and an excited alkali atom. The caesium halides are exceptional, since in these the crystal structure is different. Two extra maxima appear in caesium iodide.

The yellow coloration produced by irradiation in the absorption bands of the halides or by the action of x-rays was attributed to the production of alkali metal atoms, the formation of which is analogous to that of the latent image in the case of silver bromide. The yellow color[8] produced by irradiation of sodium chloride crystals corresponds to an absorption maximum at 4650A. This induced coloration is but slight and it is said that but few color centers are usually formed. Longer exposures or the use of more intense light sources fail to increase greatly the yield of color centers. The yields of these color centers as determined by absorption measurements give rather definite information regarding the quantum yields of the primary photoprocess. Such information can but rarely be obtained in the study of photochemical processes conducted in gaseous or liquid systems. In crystals at room temperatures, Smakula[9] found that during irradiation with very low light intensities (few quanta), the yield approached unity. With more intense irradiation, however, a condition of saturation was reached, the quantum yield dropping below unity. Under these conditions, the electron displaced was believed to return to its original location. When low intensities were used, the fewer electrons displaced throughout the crystal were thought to be able to acquire energy from the thermal motion of the crystal lattice. This energy lessened their chances of regaining their initial states.

It soon became evident that this relatively simple picture of the processes occurring in an ionic crystal required modification. The absorption of the induced color centers was observed to differ from that of the same alkali atoms in the vapor phase. It was found to be dependent upon the nature of the lattice in which the atoms were believed to be liberated. Thus, the induced maximum for the sodium salts lies at 3480A in the fluoride, at 4650A in the chloride and at 5400A in the bromide. Mollwo[10] finds the color center frequency to be inversely proportional to the square of the lattice constant. It may be displaced toward longer wave-lengths by an increase of temperature. It has also been found that the formation of appreciable amounts of the latent image or so-called F color centers depends upon the presence of defects in the lattice. The more perfect the crystal, the lower are the yields of the latent image, the electron immediately returning to the halogen atom after it has been displaced by absorption unless the energetic

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[7] Born, M., [*Z. Physik*, **79**, 62 (1932)] raised certain objections to the calculation of the wave-length of the first maximum, but it has been suggested that these may be overcome by taking into account polarization effects in the calculations of the lattice energies. See also, Klemm, W., *Z. Physik*, **82**, 529 (1933); Fues, E., *Ibid*, **82**, 536 (1933); Mayer, J. E., *J. Chem. Physics*, **1**, 270 (1933).

[8] This must be distinguished from the blue color of certain samples of rock salt which is due to the presence of colloidally dispersed sodium. Phipps, T. E., and Brode, W. R., *J. Phys. Chem.*, **30**, 507 (1926); Leroux, P., *Compt. rend.*, **188**, 904 (1929).

[9] Smakula, A., *Z. Physik*, **63**, 762 (1930).

[10] Mollwo, E., *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, **1931**, 97; **1932**, 254; *Chem. Abs.*, **26**, 5847 (1932); **27**, 665 (1933). Fröhlich, H., *Z. Physik*, **80**, 819 (1933).

conditions are modified by the presence of lattice defects, foreign atoms or surface irregularities. Smekal [11] has employed the localization of the color centers induced by irradiation as a means of studying the ultramicroscopic crevice imperfections of crystals.

The influence of the lattice structure upon the phenomenon is particularly emphasized in the newer theoretical approach to the problem. This is based upon a consideration of the energy levels of the crystal as a whole rather than of the energy levels of the isolated metal and halogen atoms or ions. The modifications in the potential energy diagrams of the isolated atoms which result when they are made to approach each other to the distances in the crystal lattice are developed mathematically. In this way there may be obtained a model analogous to that which has proved useful in recent work on the structure of metals. Such a model provides a potential energy diagram for an electron moving in the periodic force fields of a lattice.[12] Although the mathematical methods employed in this approach can be comprehended only by specialists, mention may be made of some of the results to which they have led. The sharp energy levels of the individual atoms are, in the crystal, transformed into broad bands or zones, each of which can accommodate the number of electrons required to fill in the corresponding energy level of each of the atoms in the lattice. Within each such continuous zone there are an almost infinite number of energy levels. For this reason, if a zone is only partially filled with the number of electrons which the zone can hold, these electrons are free to move as in a metal. In the alkali halide crystals, ions rather than atoms are present, since the halogen atoms have acquired from the metal atoms their loosely bound valence electrons. This means that the zone corresponding to the 4P level of the halide, *e.g.*, bromine, ions is filled with electrons.[13] On the other hand, the zone of higher energy level of the metal ions is empty (at 0°K). If by heat or light, electrons could be raised into this zone to partially fill it, these electrons would also be able to move freely throughout the crystal and render it conducting. Between these two zones there is a wide region of forbidden energy levels. In actual rather than ideal crystals, there may be additional energy levels situated just below the upper conducting energy zone. These may be due to the presence of lattice irregularities or to surface effects.

According to current theories, the color centers produced by the action of ultraviolet light or x-rays upon the alkali halide crystals are due to the presence of electrons in these localized energy levels below the conduction zone. Irradiation is believed to raise electrons to these levels from a lower level, *e.g.*, of a halide ion, by a two-stage process. It is first raised to a higher level which may or may not lie within the conducting zone. From this it drops back to the final level somewhat below the upper conducting zone. Electrons in this level are responsible for the absorption exhibited by the "latent image" or F centers. The F color centers can also be produced by directly introducing electrons from a pointed cathode [14] or by heating the crystals in an alkali metal vapor. Since different metal vapors produce the same coloration in a crystal, it appears that it is the electrons rather than, as previously supposed, the neutral atoms which are, in some manner, responsible for the color acquired by the crystals.

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[11] Smekal, A., *Physik. Z.*, **33**, 204 (1932); de Boer, J. H., *Rec trav. chim*, **56**, 301 (1937). See also, Lorenz, H., *Fortschr. Mineral., Krist. Petrog.*, **20**, 290 (1936); Blochinzew, D., *Physik. Z. Sowj*, **10**, 431 (1936).

[12] Gurney, R. W., *Proc. Roy. Soc. London*, **141A**, 209 (1933); Morse, P. M, *Phys. Rev.*, **35**, 1310 (1930); Brillouin, L., *J. physique*, **1**, 377 (1930); Kronig, R., and Penney, W. G, *Proc. Roy. Soc. London*, **130A**, 499 (1931).

[13] See, for further discussion, Webb, J. H., *J Opt. Soc. Am*, **26**, 367 (1936).

[14] Stasiw, O., *Nachr. Ges. Wiss. Göttingen Math-physik. Klasse*, **1932**, 261; Gurney, R. W., *Proc. Roy Soc. London*, **141A**, 209 (1933).

Hilsch and Pohl[15] showed that heating a crystal with F centers in hydrogen causes their gradual disappearance. At the same time a new absorption band (U band) in the ultraviolet near the long wave-length edge of the characteristic absorption band appears. The same process can be effected, although very inefficiently, by the absorption of light by the F centers. The U centers can also be produced by passing an electric current from the liquid to the crystals during their formation from the fused halide. The absorption of ultraviolet light by the U centers of the crystal reverses the optical process by which they can be formed from the F centers. As the U centers are destroyed, the F centers reappear in a one-to-one correspondence. The U centers were believed due to electrons in discrete energy levels slightly above the lower filled zone. The energetic relations between the upper conductance zone, the lower filled zone and the discrete levels representing the F and U centers have been summarized in a potential energy diagram by Tartakowsky[16] for the sodium chloride crystal. The filled and conductance zones are separated by 7.7 electron-volts, quanta of this magnitude being required to render pure crystals conducting. The F centers lie 2.65 electron-volts below the upper zone, and the U centers, 1.3 electron-volts above the lower zone.

More recently, Hilsch and Pohl[17] suggest that U centers result from the diffusion of hydrogen into the crystal and that alkali hydride molecules are formed.

A large number of investigations deal with the effects of the absorption of light by the U and F centers in crystals at various temperatures. These are primarily of physical rather than chemical interest, since they are concerned in part with photoelectric phenomena and in part, particularly in the case of crystals with foreign atom impurities, with phenomena of phosphorescence and luminescence.[18] These latter provide a basis for understanding the technically important use of luminescent substances in lighting and television. As such, they lie beyond the scope of this work.[19]

Another feature which has emerged from the use of quantum mechanics in the treatment of the absorption of light by crystals is a recognition of the fact that light energy absorbed in one portion of a crystal may be propagated throughout the lattice as an excitation wave. In other words, the excited electron and the hole it has left in the lower band may be conceived as moving about the crystal. This excitation wave may be considered, in terms of the de Broglie wave-theory of matter, as a particle called an "exciton" which moves through the crystal. This term was introduced by Frenkel in a mathematical treatment of the degradation and migration of energy in crystals.[20] Franck and Teller[21] discuss the significance of this concept in the treatment of photochemical processes induced at locations of a crystal (surfaces or disturbed lattice points) at a distance from the point at which light absorption occurs.

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[15] Hilsch, R., and Pohl, R. W., *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, **1933**, 322, 406; *Chem. Abs.*, **29**, 3237 (1935); *Z. Physik*, **87**, 78 (1933); *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse, Fachgruppe* II, **1**, 209 (1935); *Chem. Abs.*, **30**, 4763 (1936).

[16] Tartakowsky, P., *Z. Physik*, **90**, 504 (1934); Tartakowsky, P., and Poddubny, W., *Ibid.*, **97**, 765 (1935).

[17] Hilsch, R., and Pohl, R. W., *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse, Fachgruppe* II (N.F.), **2**, 139 (1936); *Chem. Abs.*, **31**, 7754 (1937); *Trans. Faraday Soc.*, **34**, 88 (1938).

[18] Hughes, A. L., *Rev. Mod. Phys.*, **8**, 294 (1936). Much of the preceding discussion has been based upon this review.

[19] For reviews, see Pohl, R. W., *Kolloid-Z.*, **71**, 257 (1935); *Proc. Phys. Soc. London*, **49**, No. 274, 3, 36 (1937); *Abhandl. Ges. Wiss. Göttingen, Math.-physik. Klasse, III*, **18**, 71 (1937); Leverenz, H. W., and Seitz, F., *J. Applied Phys.*, **10**, 479 (1939); Symposium in *Trans. Faraday Soc.*, **35**, 1 (1939).

[20] Frenkel, J., *Physik. Z. Sowj.*, **9**, 158 (1936); *Phys. Rev.*, **37**, 17, 1276 (1931); Peierls, R., *Ann Physik*, **13**, 905 (1932).

[21] Franck, J., and Teller, E., *J. Chem. Phys.*, **6**, 861 (1938).

THE SILVER HALIDES AND THE PHOTOGRAPHIC LATENT IMAGE

Present concepts of the latent image[22] are in general analogous to those developed in the treatment of the alkali halides. The importance of the photographic process led to a large amount of early work. It was indeed shown by many[23] prior to the work on the alkali halides that the primary photographic process takes place in a halogen ion rather than in silver. Before considering the recent interpretations, brief reference will be made to some of the earlier observations on the products resulting from the prolonged irradiation of the silver halides. It is interesting to recall that the existence of ultraviolet rays was first made known by the demonstration by Ritter of the ability of invisible radiations beyond the blue end of the solar spectrum to blacken silver chloride. Ritter[24] also showed that their effect could be reversed by the action of other invisible rays beyond the red. Since the absorption spectra of the bromide and iodide of silver extend into the visible, most studies have been concerned with the effects of visible light.

For a time it was considered, notably by Becquerel and by Carey-Lea, that the initial product of the action of light (latent image) was some subhalide of silver. By the study of artificial photohalides prepared by mixing and simultaneously coagulating silver and silver halide hydrosols, Luppo-Cramer cast doubt upon this. Many were the attempts to prove or disprove the existence of definite photohalides by direct quantitative measurements of the halogen evolved during prolonged irradiation of silver halides. Richardson[25] found 8 per cent of the total halogen to be liberated when 26 gms. of silver chloride under water was exposed to sunlight. Baker,[26] however, found only 14 mg. of chlorine to be evolved from 51 gms. of silver chloride after a considerable exposure to light. By the use of a special balance, Volmer[27] found silver bromide to lose as much as 40 per cent of its bromine on illumination Negative results having been recorded by Strömberg[28] and by Koch and Schrader,[29] a careful reinvestigation was made by Hartung.[30] By the use of silver bromide films on silvered vitreous silica supports on a special microbalance, he found a maximum loss of 96 per cent of the total halogen. Similar results were obtained with silver chloride. Studies of the rate of rebromination of thin silver films gave no evidence of the formation of silver subbromides. This work definitely favored the hypothesis that the formation of the latent image involves the formation of free silver.

In other attempts to solve this problem, varied techniques as microscopic studies of the effects produced by light,[31] or the alteration of the silver halide x-ray diagram[32] have been employed. The latter method gave indications of the formation of crystalline silver. The influence of various ions adsorbed on silver chloride on the liberation of chlorine by light has been studied by Schwarz and Dieffenbacher[33] In their experiments,

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[22] Webb, J. H, *J Opt. Soc Am.*, **26,** 367 (1936); "Proc 6th Summer Conference (at Mass. Inst Technology) on Spectroscopy and Its Applications," p. 157, New York, John Wiley and Sons, 1939; Gurney, R. W., and Mott, N. F., *Proc. Roy. Soc. London,* **164A,** 151 (1938)

[23] Fajans, K., and Frankenburger. W., *Z Elektrochem.*, **28,** 499 (1922), Sheppard, S. E., and Trivelli. A. P. H., *J. Phys Chem.*, **29,** 1568 (1925).

[24] Ritter, *Nicolson's J.*, **8,** 214 (1804).

[25] Richardson, A., *J. Chem. Soc*, **59,** 536 (1891).

[26] Baker, H. B., *Ibid.*, **61,** 728 (1892).

[27] Volmer, *Diss*. Leipzig, **1910,** 41. Cited by Hartung

[28] Strömberg, R., *Z wiss. Phot.*, **22,** 165 (1924); *Chem Abs*, **17,** 3838 (1923).

[29] Koch, P. P, and Schrader, F., *Z. Physik*, **6,** 127 (1921); Koch, P P., and Kreiss, B., *Ibid*, **32,** 384 (1925).

[30] Hartung, E. J., *J. Chem. Soc*, **125,** 2198 (1924); **121,** 682 (1922); **127,** 2691 (1925); **1926,** 1349

[31] Trivelli, A. P. H., and Sheppard. S. E., *J. Phys. Chem.*, **29,** 1568 (1925).

[32] Koch, P. P., and Vogler, H., *Ann. Physik,* **77,** 495 (1925); Trillat, J. J., and Motz, H., *J. Phys. Radium,* **7,** 89 (1936).

[33] Schwarz, R., and Dieffenbacher, K., *Z. anorg. Chem.*, **152,** 91 (1926).

50 mole per cent of a foreign nitrate solution was added to a silver nitrate solution which was then precipitated by an amount of sodium chloride less than sufficient to throw out all of the silver chloride. The acetate, citrate, tartrate, tetraborate and sulfate anions did not affect the rate of photodecomposition, but copper, lead, barium and thallium reduced the decomposition to 33, 32, 68 and 29 per cent, respectively, of that of silver chloride with only silver ions adsorbed.

More recently, attempts have been made to determine quantum yields for the photolysis of silver chloride. For exposures involving total absorption of the 3650A line, Feldmann and Stern[34] found a quantum yield of 0.86. The irradiation was conducted under water and the liberated chlorine determined by titration. Subsequently, they found[35] for the 3130A line a value of unity. The silver chloride used had been precipitated in the presence of sodium nitrite. The latter served to combine with the liberated chlorine and lessened the probability of a reversal of the photolysis. With more compact samples of silver chloride, the quantum yield was, however, only 0.13 in the presence of sodium nitrite and 0.20 in its absence. For precipitated silver bromide with sodium nitrite, the 3650 and 4360A lines gave yields of unity, but for silver bromide precipitated in the absence of sodium nitrite and for crystallized silver bromide in the presence of a nitrite, the yield was only 0.4. Rather similar or lower values had been reported previously by others.[36]

The yield may be affected not only by the compactness of the material, which alters the probability of the reverse reaction, but also in long continued experiments by absorption of some of the light by liberated silver atoms. MacMahon and Chatterji[37] measured the absorption of oxygen by irradiated silver bromide and chloride in a tube containing gold as halogen acceptor. The oxygen is absorbed by the dispersed silver resulting from the photolysis.

During the formation of the latent image, the silver halides exhibit photoconductivity. The absorption band of silver bromide in the visible has a minimum energetic separation from the unfilled upper conductance band of the order of three electron-volts. Electrons raised into this band give rise to conductance.[37a] An approximate agreement between the sensitivity curves for photoconductance and for the photographic effects was observed by Arrhenius,[38] indicating according to present conceptions, that the liberation of an electron by light absorption may be concerned also with the formation of the latent image. Some discrepancies between the curves were noted by Coblentz,[39] but Toy[40] and co-workers explain these as due to the fact that the photoconductance experiments were made on large pure silver bromide crystals and the photographic ones on fine crystals in gelatin. Sheppard and Vanselow[41] calculated that the photoelectrons have in the lattice a mean free path of the order of 10^{6} cm.

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[34] Feldmann, P., and Stern, A., *Naturwiss.*, **16**, 539 (1928); *Z. physik. Chem.*, **12B**, 449, 467 (1931).

[35] *Z. physik. Chem.*, **26B**, 45 (1934). See, however, Plotnikow, I., *Phot. Korr.*, **67**, 199 (1931), *Chem. Abs.*, **26**, 1861 (1932).

[36] Eggert, J., and Noddack, W., *Z. Physik*, **31**, 922, 942 (1925); Eggert, J., *Z. Elektrochem.*, **32**, 491 (1926)

[37] MacMahon, P. S., and Chatterji, A. C., *Proc. 15th Indian Sci. Congr.*, **1928**, 138, *Chem. Abs.*, **25**, 2922 (1931).

[37a] For a quantum-mechanical treatment of conductance, see Fowler, R. H., *Proc. Roy. Soc. London*, **140A**, 505 (1933); **141A**, 56 (1933).

[38] Arrhenius, S., *Sitzb. Akad. Wiss. Wien*, **96**, 831 (1887); Scholl, H., *Ann. Physik*, **16**, 193, 417 (1905); Wilson, W., *Ibid.*, **23**, 107 (1907).

[39] Coblentz, W. W., *Bur. Standards Bull.*, **18**, 489 (1922). This section is based in part upon a review by Webb, J. H., *J. Opt. Soc. Am.*, **26**, 367 (1936).

[40] Toy F. C., *Nature*, **120**, 441 (1922); *Proc. 7th Intern. Congr. Phot.*, 14 (1928); Toy, F. C., and Harrison, G. B., *Nature*, **123**, 679 (1929); *Proc. Roy. Soc. London*, **127A**, 613, 629 (1930).

[41] Sheppard, S. E., and Vanselow, W., *J. Phys. Chem.*, **33**, 250 (1929); Sheppard, S. E., *Phot. J.*, **60**, 397 (1928).

As in the case of the alkali halide crystals, the formation of the latent image may be demonstrated optically. The absorption spectrum of silver bromide extends from about 4700A to the shorter wave-lengths and exhibits a maximum at about 2200A. It differs from the spectra of the alkali halides in lacking sharp maxima and minima, although there are indications of their existence. The latent image formed by exposures to the low intensities ordinarily used in photography is not visible, but Hilsch and Pohl[42] showed that by the use of thicker crystals and greater exposures it could be detected as an induced band in the infrared with a maximum at 6900A. The absorption spectra of the original crystal and that of the latent image may partially overlap and that of the latent image may tend to become complex as compared with those encountered in the alkali halides. This may be ascribed to a tendency for the liberated silver atoms to become coagulated.[43] Hilsch and Pohl calculated from dispersion theory and the observed absorption of the latent image that in both the photographic plate and in irradiated alkali halide crystals, the latent image is due to a concentration of but one color center in 10^6 to 10^7 salt molecules. The quantum yield amounts to about 0.33 to 0.4 color centers per photon under the usual exposure conditions. Blair and Leighton[44] have given an equation expressing the rate of formation of the latent image.

It has been assumed recently that the latent image corresponds in a general way to the F centers of the alkali halides. According to this view the latent image would represent electron energy levels rather than silver atoms. The manner in which such electronic excitation levels occasion the liberation and coagulation of silver atoms is as yet speculative.[45]

Theories of Sensitivity. It has been stated that the light-sensitivity of the silver halides does not coincide with their absorption curves, since it has a maximum in the short visible, and drops off in the ultraviolet where the absorption curve is still rising rapidly. A small hump observed by Fesefeld[46] at about 4300A in the absorption spectrum of silver iodide does, however, coincide with the region of maximum sensitivity of that salt. There is also some discrepancy between the long-wave thresholds for absorption and photographic action. In part this may be due to the fact that methods for detecting the formation of a latent image by subsequent development are more sensitive than those for measuring the silver halide light absorption curve. Before the development of the theories discussed in connection with the alkali halides, attempts were made to relate the sensitivity threshold to the energy required to remove electrons from the halogen ions of the normal crystal lattice. Wave-lengths longer than those calculated proved, however, to be effective. Frankenburger and Fajans[47] suggested that submicroscopic flaws in the crystal lattice might serve to lessen the energy required. Pauling[48] proposed to calculate the threshold wave-length by deducting from the sum of the electron affinity of the halogen and the coulombic energy of the lattice a term representing the work done when an electron is brought into the crystal from an infinite distance. He believed this latter quantity a function of the diamagnetism of the crystal. It may be recalled that, in the case of the alkali halides, Hilsch and Pohl had used the ionization potential of the metal as the energy quantity to be deducted. They have also suggested that during the ripening of a photographic emulsion there may be produced centers analogous to the U centers of alkali halide crystals. Electrons in these centers could be lifted to the conductance zone by smaller quanta than those needed by electrons in the lower filled level. It appears likely that continued development of the newer quantum mechanical theories may serve to increase greatly our knowledge of the mechanisms involved.[49]

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[42] Hilsch, R., and Pohl, R. W., *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, **1930**, No. 2, 176; *Chem. Abs.*, **25**, 884 (1931); *Z. Physik*, **64**, 606 (1930) For analogous results on silver halide grains, see Kirillow, E. A., *Z. wiss. Phot.*, **26**, 235 (1929); *Chem. Abs.*, **23**, 1829 (1929); Eggert, J., and Schmidt, R., *Z. Physik*, **48**, 541 (1928).

[43] See Löhle, F., *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, **1933**, 271; *Chem. Abs*, **28**, 973 (1934); Savost'yanova, M. V., and Toporetz, A., *Compt rend acad. Sci. (U.R.S.S.)*, **2**, 225 (1934); *Chem. Abs.*, **28**, 5340 (1934).

[44] Blair, J. M., and Leighton, P. A., *J. Phys. Chem.*, **36**, 1649 (1932); *Phot. Korr. (Suppl.)*, **69**, 27 (1933).

[45] See Berg, W. F., *Trans. Faraday Soc.*, **35**, 445 (1939); Berg, W. F., and Mendelssohn, K., *Proc. Roy. Soc. London*, **168A**, 168 (1938).

[46] Fesefeld, H., *Z. Physik*, **67**, 37 (1931).

[47] Frankenburger, W., and Fajans, K., *Z. physik. Chem.*, **105**, 255, 273 (1923). Pressure may prevent the formation of the latent image according to Poindexter, F. E., *J. Opt. Soc. Am.*, **21**, 59 (1931).

[48] Pauling, L., *Phys. Rev.*, **34**, 954 (1929).

Mention must also be made of the observation that the sensitivity of a photographic emulsion is related to the presence in the grains of specks of a foreign substance.[50] Development of an exposed grain is known to start at these specks. These were at one time regarded as silver sulfide, serving the function of forming the anodes of minute photoelectric cells.[51] At present, they are thought to be due to the presence of organic sulfur compounds, derived from the gelatin of the emulsion.[52]

The more recent theories regard the function of the specks as that of concentrating the silver atoms liberated by the light. It may be that light absorbed at other portions of the grain moves through the grain as an "exciton" toward the disturbing speck.[53] A radically different theory, due to Stock,[54] denies the need for postulating sensitivity specks and regards the latent image as excited silver atoms on blocks of the grain, which is assumed to possess a mosaic structure.

Much effort has been expended in determining the properties which render a latent image developable. Toy and Edgerton[55] found the relative number of developable centers produced in silver bromide grains by exposure to monochromatic light to be proportional to the number of quanta absorbed by the silver bromide. Weigert[56] conceives of the latent image as complex micelles of silver halide, water, gelatin and "Ursilber" of increased energy content. This energy, which he believes may represent a summation of many quanta, is supposed to activate the developer molecules.

Trivelli[57] claims that the larger the specks originally present in an unexposed film, the smaller the amount of silver which needs to be added to it during exposure in order to produce a developable latent image. Sheppard[58] finds that the number of silver atoms produced by exposure and the preexisting nuclei are together too small to support the hypothesis of a minimum critical size for development centers. He believes the state and more particularly the orientation of the silver atoms is a more important determinant of the developability of nuclei than their size.[59] Reinders and Hamburger,[60] however, maintain that the smallest developable aggregates consist of three, four or more silver atoms or silver sulfide molecules.

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[49] Gurney, R. W., and Mott, N. F., *Proc. Roy. Soc. London*, **164A**, 151 (1938); Berg, W. F., *Trans. Faraday Soc.*, **35**, 445 (1939); Berg, W. F., and Mendelssohn, K., *Proc. Roy. Soc. London*, **168A**, 168 (1938).

[50] Wightman, E. P., Trivelli, A. P. H., and Sheppard, S. E., *J. Frank. Inst.*, **194**, 485 (1922); Sheppard, S. E., and Wightman, E. P., *Ibid.*, **195**, 337 (1923); Sheppard, S. E., Wightman, E. P., and Trivelli, A. P. H., *Ibid.*, **196**, 653, 779 (1923); **198**, 507, 629 (1924); **200**, 335 (1925); Sheppard, S. E., Trivelli, A. P. H., and Loveland, R. P., *Ibid.*, **200**, 51 (1925); Clark, W., *Phot. J.*, **48**, 91 (1924); Toy, F. C., *Phil. Mag.*, **44**, 352 (1922); Sheppard, S. E., and Trivelli, A. P. H., *Phot. Korr.*, **64**, 145, 173, 242, 273 (1928); Svedberg, T., *Z. wiss. Phot.*, **20**, 36 (1920); *Chem. Abs.*, **15**, 2393 (1921); *Phot. J.*, **62**, 183, 186, 310 (1922).

[51] Trivelli, A. P. H., *J. Frank. Inst.*, **204**, 649 (1927); **205**, 111 (1928); *Phot. J.*, **68**, 67 (1928). *Contra*, Harrison, G. B., *Phot. J.*, **71**, *Sci. Tech.* (*Suppl.*), 1 (1931).

[52] Sheppard, S. E., *Phot. J.*, **49**, 380 (1925); *Nature*, **123**, 979 (1929); "Colloid Symposium Monograph," **3**, 76, New York, Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1925; Price, T. S., and Rawling, S. O., *Nature*, **116**, 281 (1925); Price, T. S., *Phot. J.*, **65**, 298 (1925); Silberstein, L., *Phil. Mag.*, **5**, 464 (1928).

[53] Compare Hecht, K., *Z. Physik*, **77**, 235 (1932).

[54] Stock, L. W., *Skrifter Norske Videnskaps-Akad Oslo I, Mat.-natur. Klasse*, **No. 10**, 1-82 (1938); *Chem. Abs.*, **33**, 2827 (1939).

[55] Toy, F. C., and Edgerton, H. A., *Phil. Mag.*, **48**, 947 (1924).

[56] Weigert, F., *Z. wiss. Phot.*, **29**, 191 (1930); **30**, 217 (1931); *Chem. Abs.*, **25**, 1170 (1931); **26**, 3739 (1932); *Phot. Korr.*, **70**, (*Suppl.*), 41 (1934); *Naturwiss.*, **19**, 969 (1931).

[57] Trivelli, A. P. H., *Nature*, **126**, 760 (1930).

The relation between the silver produced on development to the silver produced in the primary photoprocess is known as the development factor. It decreases with the grain size, being 3×10^8 for a grain mass of 6×10^{-12} and 10^3 for a grain mass of 10^{-16}. This is because the larger the grain, the greater the probability that it will contain a sensitizing nucleus of a certain size. Further details[61] of the theory of the sensitivity of photographic emulsions lie beyond the scope of this work.

HERSCHEL EFFECT

In 1839, Sir John Herschel observed that red light causes a fading of the direct photochemical image produced by illuminating silver chloride. For a considerable time, this was regarded as an effect due to oxidation, but the observations of Leszynski[62] cast doubt on this, and, according to Trivelli,[63] more recent workers regard it as due to a photochemical bleaching of the latent image. Absorption of light by the latent image causes a photoconductivity, which tends to restore the original condition of the lattice by removing an electron from the silver atom and restoring it to the halogen. In the case of the alkali halides, the absorption of light by the latent image has two effects, the predominance of either of which is conditioned primarily by the nature of the crystal and its temperature. Bleaching predominates in the silver halides.[64] Lüppo-Cramer[65] has shown that the Herschel effect is not entirely confined to the red end of the spectrum, but may also occur when the intensity is small with yellow, green and even with blue light.

SENSITIZATION

Sensitization to Longer Wave-Lengths. It has been observed that a silver bromide hydrosol containing adsorbed silver ion, in contrast to one with adsorbed bromide ion, shows increased absorption in the yellow and green regions. The absorption curve as a whole is shifted toward the longer wave-lengths by 150 to 200A, and at the same time the spectral sensitivity is shifted toward the longer wave-lengths.[66] Similar effects are also observed in gelatin emulsions. The thallous ion has a similar effect half as great.[67] To some extent the latent image

[58] Sheppard, S. E., *Phot J.*, **71**, 313 (1931); *Chem. Abs.*, **25**, 5631 (1931).

[59] See also Arens, H., *Z. wiss. Phot.*, **30**, 49 (1931); Sheppard, S. E., *Ber. 8th Intern. Congr Phot., Dresden*, **1931**, 13; *Chem. Abs.*, **27**, 237 (1933).

[60] Reinders, W., and Hamburger, L., *Z. wiss. Phot.*, **31**, 32, 265 (1932), *Chem Abs.*, **26**, 4545 (1932); **27**, 2641 (1933).

[61] Fredenhagen, K., and Wellmann, M., *Z. physik. Chem*, *Bodenstein Festband*, 135 (1931); James, T. H., *J. Chem Physics*, **2**, 132 (1934); Blair, J M., and Hylan, M C, *J. Opt. Soc. Am.*, **23**, 353 (1933); James T. H. and Coleman, J. J., *J Chem Phys*, **2**, 483 (1934).

[62] Leszynski, W., *Z. wiss. Phot.*, **24**, 275 (1926); *Chem Abs*, **21**, 863 (1927).

[63] Trivelli, A. P. H., *J Frank. Inst.*, **207**, 765 (1929).

[64] Smakula, A., *Z. Physik*, **59**, 603 (1929).

[65] Lüppo-Cramer, *Phot Korr.*, **64**, 108 (1928).

[66] Fromherz, H., *Z. physik. Chem.*, **1B**, 324 (1928), Fajans, K., Fromherz, H., and Karagunis, G, *Z. Elektrochem.*, **33**, 548 (1927); Fajans, K, and Karagunis, G., *Naturwiss*, **17**, 274 (1929); Fajans, K., and Steiner, W., *Z. physik. Chem*, **125**, 275, 307 (1927).

[67] Fromherz, H., and Karagunis, G., *Z. physik. Chem.*, **1B**, 346 (1928).

itself may also act to sensitize a plate to longer wave-lengths.[68] These effects, however, are all of relatively little importance in comparison with the sensitizing effects which may be brought about by certain organic dyestuffs. These can be used to alter the natural sensitivity of photographic emulsions so as to render them, either approximately equally sensitive to all of the visible wave-lengths or to extend the range of sensitivity into the infrared or to the shorter ultraviolet regions.

In 1873, Vogel noticed that certain dyes, such as Corallin, which has an absorption band in the yellow-green, sensitized plates to the region which these dyes absorb. The Isochromatic plates of fifty years ago, sensitized with eosin, were the first color-sensitive plates to have been generally used. Many other dyes have since been found more satisfactory. Particularly important are the isocyanine dyes, as ethyl red, carbocyanines, including pinacyanol, and a number of others as kryptocyanine and neocyanine. The use of such dyes has made possible the advances in long-range, haze-penetrating, infrared photography.

The theory underlying the action of these dyes is still somewhat obscure. The range of sensitization and the absorption spectra of the dyes do not coincide as closely as had been at first thought to be the case. It has, however, been suggested that the dyes when adsorbed on the halide grains may have their absorption spectra shifted.[69] In some instances obscure chain reactions may be set up. Not all dyes sensitize when adsorbed. A common constitutional factor in the effective ones appears to be the existence of either two oxygen or two nitrogen atoms in two states of valency, joined by a chain of conjugated double bonds.[70]

Rabinovich has suggested that in solid systems the energy evolved in the photoöxidation of the adsorbed sensitizer by atmospheric oxygen may be utilized in the decomposition of the crystals to which it is adsorbed.

Ultraviolet Plates. Duclaux and Jeantet [71] suggested that a photographic plate may be sensitized to the extreme ultraviolet by the application of a thin coating of oil. Lyman [72] believes the process does not yield results comparable with the Schumann procedure (Chapter 1), but agrees that its possibilities have not been fully explored. The changes in sensitivity and contrast produced by coating plates of various brands with five different fluorescent oils, in the region of 2200-3800A have been studied by Harrison [73] and by Söderman,[74] the latter finding only Schumann plates to be satisfactory in the range 50-500A. A 0.5 per cent solution of vaseline in light petroleum may be employed.[75] Citric acid and salicylates have also been used.[76] Eggert and Arens [77] have added to ordinary plates a layer containing a wetting agent and a substance such as fluorene or anthracene which fluoresces in the ultraviolet region. The purpose of the wetting agent, saponin or Turkey-red oil, is to aid in the removal of the fluorescent substance in the development bath. Rathenau[78] suggests impregnating the plate with a filtering dye which absorbs light of fairly long wave-length and then covering it with a sensitizing oil film which acts on short wave-lengths unabsorbed by the dye. Among the dyes proposed were nitrosodimethylamine, methyl orange, fuchsine. As the sensitizer, Cenco pump oil 11021B could be used.

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[68] Eggert, J., and Noddack, W., *Z. Physik,* **31**, 942 (1925). *Synthetic Organic Chemicals, Eastman Kodak Co.,* Dec. 1927. For the earlier observations, including those of Becquerel, Lüppo-Cramer and of Fajans, see Mees, C E K., *J Frank Inst*, **201**, 525 (1926)

[69] See also Rabinovich, A J., *Sci. ind. Phot.*, **6**, 288 (1935); *Chem. Abs.*, **30**, 3343 (1936).

[70] For further studies of the sensitizing action of erythrosine on colloidal solutions of silver bromide, see Bokinik, Y I, and Il'ina, Z A., *Acta Physicochim. U.R.S.S*, **3**, 383 (1935) *Chem. Abs.*, **30**, 3297 (1936). For the recent development of sensitization theories, Wahl, H., *Chim. et Ind.*, **36**, 16 (1936); Rabinovich, A. J., *Acta Physicochim. U.R.S.S.*, **3**, 368 (1935); *Chem Abs.*, **30**, 3343 (1936); Webb, J. H., *J. Opt Soc. Am.*, **26**, 367 (1936); Bokinik, Y. A., and Il'ina-Bagdasar'yan, Z. A., *J. Phys. Chem. U.R S.S.*, **11**, 197 (1938); *Chem. Abs.*, **33**, 3277 (1939); Bagdasar'yan, K. S., *Acta Physicochim. U.R S S.*, **9**, 205 (1938), *Chem Abs*, **33**, 5759 (1939); Sheppard, S. E., Lambert, R. H., and Walker, R. D., *J. Chem. Phys.*, **7**, 426 (1939).

[71] Duclaux, J., and Jeantet, P., *Science*, **58**, 48 (1923); *J. phys. radium*, **2**, 156 (1921); *Chem. Abs.*, **15**, 2798 (1921).

[72] Lyman, T., *J. Frank Inst*, 5560, May, **1926**.

[73] Harrison, G. R., *J. Opt. Soc. Am.*, **11**, 113 (1925).

[74] Söderman, M., *Z. Physik*, **67**, 790 (1931).

[75] Beach, A. C. G., *Nature*, **123**, 166 (1929).

[76] J. and J. F. Thovert, *Bull. seances soc. franç. phys.*, **1932**, 158; *Chem. Abs.*, **27**, 5662 (1933).

[77] Eggert, J., and Arens, H., German P. 640,157, Dec. 23, 1936. (To I. G. Farbenindustrie); *Chem. Abs.*, **31**, 2112 (1937).

Details of the sodium salicylate method, including the sensitometry of the plates so treated, have been given by Montagne and Ricard,[79] Kiu,[80] and Terrien.[81]

Ethyl dihydrocollidinedicarboxylate has been proposed.[82] Sheppard and Vanselow[83] use a silver salt of 1-*p*-sulfophenyl-3-methyl-5-pyrazolone, or related compounds. A number of solutions enumerated by Allen and Franklin[84] for sensitizing plates to radiations shorter than 2500A are shown in Table 20. The aqueous

Table 20. Substances Used for Ultraviolet Sensitization of Plates.

	Chemical Name	Trade Name	Solvent	Approximate Concentration	Remarks
1.	1-naphthylamine-4-sulfonic acid	Naphthionic Acid	Water	2%	Add 4% Na_2CO_3
2.	2-naphthylamin-1-sulfonic acid	Eastman's T386	"	2%	"
3.	2-naphthylamine-6-sulfonic acid	Bronner's Acid	"	2% (sat)	"
4.	2-naphthylamine-6,8-disulfonic acid	Amino G Acid	"	4%	"
5.	2-naphthol-6,8-disulfonic acid	G Acid	"	4%	"
6.	α-naphthylamine		Ethyl acetate	2%	Add 4cc. alcoholic solution of white shellac per 100 cc.
7.	Fluorene		"	2.5%	"
8.	Carbazole		"	2%	"
9.	Ethyl carbazole		"	2%	"

solutions are merely applied to the plates for a few seconds, after which the plates are allowed to dry in a vertical position. Just before development, the plates should be rinsed with water. When water-insoluble organic substances are used, these should be removed before development by means of acetone. The same treatment should be used on plates treated with fluorescent oils or Eastman sensitizer.

In a photosensitive layer sensitive to the ultraviolet, Sheppard and Eberlin[85] use for application to paper dextrose and an oxygen-containing compound of a metal of the sixth periodic group having an atomic weight between 90 and 200, such as sodium tungstate or molybdate.

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[78] Rathenau, G., *Physica*, **2**, 840 (1935).

[79] Montagne, R., and Ricard, R., *Compt rend.*, **202**, 477 (1936).

[80] Kiu, T., *Compt. rend.*, **201**, 1348 (1935); *Sci. ind. phot.*, **8**, 1 (1937); *Chem. Abs.*, **31**, 2948 (1937).

[81] Terrien, J., *Compt rend.*, **202**, 211 (1936)

[82] Burroughs, R. E., U. S. P. 1,880,411, Oct. 4, 1933. (To Eastman Kodak Co.). *Chem. Abs.*, **27**, 675 (1933).

[83] Sheppard, S. E., and Vanselow, W., U. S P 2,066,582 (To Eastman Kodak Co), *Chem. Abs.*, **31**, 962 (1937).

[84] Allen, A. J., and Franklin, R. G., *J. Opt. Soc Am.*, **22**, 469 (1932).

[85] Sheppard, S. E., and Eberlin, L. W., U. S. P. 1,934,451, Nov. 7, 1934 (To Eastman Kodak Co.); *Chem. Abs.*, **28**, 426 (1934).

Russell Effect. It has long been known that a very great number of substances are capable of affecting a photographic plate in the dark (Russell effect). An exhaustive review of the work in this field has been given by Keenan,[86] who concludes that, in general, a vapor passes from the active substance to the plate, and that it is of the nature of hydrogen peroxide or an organic peroxide.

THE WEIGERT EFFECT

It was shown by Weigert [87] that exposure of very thin layers of silver chloride (when sensitized by free silver produced by a previous exposure to ordinary light) to plane polarized light renders the layer color-adapted and dichroic, that is, causes it to exhibit different extinction coefficients in polarized light according to the direction of the plane of polarization. This is a sign of a definite anisotropy in the layer. The optical axis of the photoanisotropic system is always parallel to the plane of the electric vector. After a preliminary exposure to polarized light, the orientation set up determines or orients a subsequent decomposition effected by non-polarized light. This Weigert termed induced photoanisotropy. Zocher and Coper [88] have obtained the effect by the use of circularly polarized light. Weigert regarded the effect as due to definite alterations in the shape of complex silver micelles. It has, however, been shown by Cameron and Taylor [89] that the effect can be produced in single crystals of silver chloride previously rendered blue by exposure. Both silver and a silver halide lattice are necessary, but gelatin or other components of photographic emulsions or the gel state are not essential. It is suggested that suitably dimensioned and oriented silver particles can respond to polarized light by ejecting electrons in a definite direction. These reform silver from the silver ions in the lattice, the chlorine being assumed to migrate.

Weigert also observed the phenomenon in the photodecomposition of light-sensitive dyes embedded in gelatin.[90] In cases in which there is rigidity, either of a crystal lattice or of a gel, photoanisotropy effected by polarized light may persist. In gaseous or liquid systems, in which the photochemical products are rapidly disoriented by collisions, it is evanescent.[91]

OTHER SILVER COMPOUNDS

Wave-lengths longer than 2500A are said not to reduce silver nitrate in pure gelatin, unless there is present 10^{-5} gram mole of potassium chloride or bromide per liter of gelatin. Even eosin or rhodamine-silver nitrate-mannitol mixtures are stable in ultraviolet light if they have previously been subjected to ultrafiltration.[92]

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[86] Keenan, G. L., *Chem. Rev.*, **3**, 95 (1926).

[87] Weigert, F., *Verhand. deut. physik. Ges.*, 21, 479 (1919); summarizing statements in *Naturwiss.*, **9**, 583 (1921); **16**, 613 (1928); 19, 969 (1931); *Z. physik. Chem.*, **3B**, 377 (1929); **4B**, 239, 258 (1929); **18B**, 73 (1932); see also Nikitine, S., *Compt. rend.*, **204**, 973 (1937); **208**, 513, 643 (1939); Cherduintzev, S., *Acta Physicochim. U.R.S.S.*, **3**, 355 (1935); *Chem. Abs.*, **30**, 2110 (1936); Ungar, G., *Compt. rend.*, **208**, 337 (1939).

[88] Zocher, H., and Coper, K., *Z. physik. Chem.*, **141**, 217 (1929); **132**, 313 (1928). See also Cotton, A., *Compt. rend.*, **189**, 599 (1929).

[89] Cameron, A. E., and Taylor, A. M., *J. Opt. Soc. Am.*, **24**, 316 (1934).

[90] See also Nikitine, S., *Compt. rend.*, **208**, 805 (1939).

[91] Ghosh, J. C., and Banerjee, T., [*Kolloid-Z.*, **86**, 372 (1939)] have recently reviewed extensive experiments on the production of circular dichroism in various inorganic sols by irradiation with circularly polarized light during their formation.

[92] Bokinik, Y. A., *J. Phys. Chem. (U.S.S.R.)*, **11**, 190 (1938); *Chem. Abs.*, **33**, 4130 (1939).

A solution containing starch, silver nitrate and an excess of potassium iodide rapidly becomes blue on exposure to light. Since the reaction is not observed in the presence of an excess of the silver ion, it may be assumed that the iodine liberated is derived from potassium iodide adsorbed on silver iodide, the latter exerting an enormous accelerating influence on the oxidation of the former.[93]

According to Ishii,[94] the compound $AgKI.2H_2O$ exists as asbestos-like crystals which change from peach color to dark purple under sunlight and to dark gray under mercury arc light. Rather similar changes are also observed in the colorless compounds $2AgI.KI.1/2H_2O$ and $2AgI.KI.2H_2O$. The compound $4AgI.KI.2C_3H_6O$ is not affected by sunlight but changes from colorless to a peach color under the mercury arc. Ag.2KI and Ag.6KI are unaffected by light.

Arens and Eggert[95] found sensitive gelatin emulsions of silver acetylide, azide or oxalate to be developable under suitable conditions. Each of the three salts is white and absorbs in the same region of the ultraviolet as does silver chloride. After a long exposure of the acetylide, a residue of carbon is found on dissolving away the silver. Nitrogen separates directly from the azide on exposure to light of high intensity, but this does not occur as a result of a correspondingly longer exposure to light of a lower intensity. Possibly in this case hydrogen azide is formed. Contrary to what might be expected from their endothermic nature, the amount of silver which separates directly on exposure of either of these three salts is of the same order of magnitude as that formed from silver chloride.

There are photographic processes which do not employ silver salts. Among these are the bleaching of photosensitive dyes, generally by oxidation, diazo-processes in which after the loss of nitrogen the remaining residue of the diazo-body can be coupled to form a dye, alkaline bichromate processes in which there forms a chromic oxide capable of tanning gelatin and certain iron processes.

Gelatin impregnated with ferric chloride gives a white image when exposed under a negative.[96] Mixtures of tartaric acid and ferric salts with selenious acid or with potassium tellurate are reduced in light with the formation of amorphous selenium or tellurium. Sensitive papers utilizing this behavior have been prepared.[97] The selenium paper gives a bright red and the tellurium paper a black to brown tone. The development and fixation may be carried out with a dilute solution of hydrochloric acid, with the addition, in the case of the tellurium paper, of stannous chloride to prevent the destruction of the image by the unchanged ferric chloride.

The Blackening of Lithopones

The white pigment lithopone, a mixture of zinc sulfide and barium sulfate, is prone to blacken on exposure to ultraviolet radiations from an arc or in sunlight. Eibner[98] attributed this to an interaction of metallic impurities with the sulfide pigment. Roches[99] attached much importance to the presence of chlorides, but did not find iron, cadmium, cobalt or manganese harmful. Brickwedde[100] believed soluble salts whose sulfides are black to promote the change. The elimination of impurities from the raw materials employed in the manufacture of this pigment has greatly increased its light stability.[101] It is, nevertheless, true that even carefully purified Wurtzite, zinc blende and unignited zinc sulfide, in the presence of water, blacken when subjected to ultraviolet rays.[102] In an atmosphere of hydrogen, the decomposition products contain hydrogen, zinc, sulfur, and the zinc and sulfate ions. Electrolytes increase the light-sensitivity. By irradiating a suspension of zinc sulfide in water, Job and Emschwiller[103] had previously obtained sulfur, zinc and hydrogen.

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[93] Hiller, W., *Z anorg. Chem.*, **219**, 313 (1934); *Brit. Chem. Abs.*, **1934A**, 1183.

[94] Ishii, S., *Repts. Osaka Imp. Ind. Research Inst. Japan*, **11**, No. 20 (1931); *Chem Abs.*, **25**, 5362 (1931).

[95] Arens, H., and Eggert, J., *Phot. Korr.*, **67**, **No. 8**, 17 (1931); *Veröffentl. wiss. Zentral-Lab. Phot. Abt.* AGFA **3**, 67 (1933); *Chem. Abs.*, **26**, 1529 (1932); **28**, 3012 (1934); Moskovich, S. M., *J. Phys. Chem* (*U.S.S.R.*), **12**, 460 (1938); *Chem. Abs.*, **33**, 4892 (1939).

[96] Schommer, F., *Atelier Phot.*, **33**, 91 (1926); *Chem. Abs.*, **21**, 538 (1927).

[97] Pavolini, T., *Giorn. Chim. Ind. Appl.*, **12**, 72 (1930); *J. Soc. Chem. Ind.*, **1930**, Suppl. 533.

[98] Eibner, A., *Chem. Ztg.*, **49**, 345, 370 (1925). The darkening of red mercuric sulfide was also discussed.

[99] Roches, C., *Rev. chim. ind.*, **31**, 109 (1922); *Chem. Abs.*, **16**, 3217 (1922). See also Schleede, A., Herter, M., and Kordatzki, W., *Z. physik. Chem.*, **106**, 386 (1923).

It was believed by Mass and Kempf[104] that the lattice structure is essential to the blackening and that amorphous freshly precipitated zinc sulfide or zinc sulfide which has been ground in a mortar is insensitive to light. Such samples must be subjected to heat treatment to convert them into phosphors before they will blacken.[105] Only luminescent samples exhibit the phenomenon, possibly because neutral atoms of zinc, cadmium or silver must be present in the interstices of the lattice.[106] Mass and Kempf attributed the change in the zinc sulfide to a process analogous to that which occurs during the exposure of silver bromide; zinc and zinc disulfide were assumed to be formed, the zinc appearing in finely divided form on the surface of the mass. It may be that in the primary process, electrons pass from a sulfide ion on the surface of the crystal lattice and discharge a neighboring zinc ion. Irradiation produces photoconductivity, but there are differences in the spectral sensitivity curves for blackening and for photoconductivity. Gordon, Seitz and Quinlan[107] have speculated regarding the nature of the two-quantum shifts of electronic energy-levels involved. They believe the blackening occurs at the surface as an electrolysis of zinc sulfide in solution in the surface moisture under the electromotive force produced by the optically-formed Zn^+ and S^- ions. The liberation of hydrogen noted by Job and Emschwiller has not yet been interpreted in terms of the newer theories.

Glycerol and other polyatomic alcohols have been believed to protect lithopones.[108] Waterglass is also said to be effective.

It was observed by Mass and Kempf that blackened lithopone brightens in darkness owing to the oxidation of metallic zinc, but remains black if no oxygen is present. The rate of bleaching of darkened lithopone and the photoelectric effect of the latter are similar to the behavior of samples of lithopone upon the surface of which zinc has been distilled.[109]

To determine the relative effectiveness of various wave-lengths, Pfund[110] rubbed a sample in water and covered it with a quartz plate. The specimen was then mounted in the focal plane of a quartz spectrograph, so that the entire spectrum from an iron arc was projected upon the lithopone surface, which, by darkening indicated the spectral regions of greatest effectiveness. Wave-lengths longer than 3200A showed very little darkening. By the use of monochromatic light of constant intensities, it was shown that the sensitivity of lithopone is almost nil in the visible spectrum, and rises to a high value in the ultraviolet near 2900A, remaining practically constant at shorter wave-lengths. All samples of lithopones tested by Pfund showed the same general type of sensitivity curves. These curves were obtained by plotting against the wave-lengths the reciprocals of the time in seconds required to produce a visible darkening by these wave-lengths, the intensity being maintained constant. Brickwedde, employing this method, found very different results, the sensitivity beginnig at 3700A and showing a subsidiary maximum at 3130A.

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[100] Brickwedde, F. G., *J. Opt. Soc. Am.*, **14**, 312 (1927).

[101] Eibner, A., *Farben Ztg.*, **30**, 2600 (1925); *Chem. Abs.*, **19**, 3601 (1925).

[102] Platz, H., and Schenck, P. W., *Z. angew. Chem.*, **49**, 822 (1936).

[103] Job, A., and Emschwiller, G., *Compt. rend.*, **177**, 313 (1923); see also Weiser, H. B., and Garrison, A. D., *J Phys. Chem.*, **31**, 1237 (1927).

[104] Mass, E., and Kempf, R., *Z. angew. Chem.*, **36**, 293 (1923); *J. Chem. Soc.*, **124**, ii, 491 (1923).

[105] See, however, Streck, E., *Ann Physik*, **34**, 96 (1939); **35**, 58 (1939).

[106] Seitz, F., *J. Chem. Phys.*, **6**, 454 (1938); Brusilowskii, A. M., Sigal, F. S., and Kabanova, E. Y., *Lakokrasochnuyu Za*, **1935**, No. 3, 11; *Chem. Abs.*, **31**, 6485 (1937); Brusilowskii, A. M., *Org. Chem. Ind. (U.S.S.R.)*, **5**, 493 (1938); *Chem. Abs.*, **33**, 883 (1939).

[107] Gordon, N. T., Seitz, F., and Quinlan, F., *J. Chem. Phys.*, **7**, 4 (1939); compare Stobbe, H., *Z. wiss. Phot.*, **29**, 209 (1930); *Chem. Abs.*, **25**, 1441 (1931).

[108] Nishizawa, Y., *J. Tokyo Chem. Soc.*, **41**, 1054 (1920); *Chem. Abs.*, **15**, 1407 (1921); see also, British P. 156,971, Nov. 25, 1919; Gardner, H. A., and Holdt, P. C., *Paint Mfrs. Assn. Circ.*, **194**, 174 (1924); *Chem. Abs.*, **18**, 910 (1924).

[109] Brickwedde, F. G., *J. Opt. Soc. Am.*, **14**, 312 (1927). See also Goshorn, J. C., and Black, C. K., *Ind. Eng. Chem.*, **21**, 348 (1929).

[110] Pfund, A. H., *Proc. Am. Soc. Testing Materials*, **23**, II, 375 (1923).

In testing lithopones, Gardner and Holdt [111] use either an exposure to sunlight, or as an accelerated test, to the rays of a mercury or iron arc. When the mercury arc is used, the pigment is exposed as a dried oil paint film on a palette submerged in a shallow layer of water to reproduce a condition of constant humidity. The test should be carried out on the pigment ground in the vehicle in which it is intended to be used. The acid value of the oil medium used has a marked effect, increasing acid values in a series of alkali-refined linseed and tung oils diminishing but not entirely inhibiting the darkening of the pigment. When employing the rays from an iron arc, the lithopone paste is exposed behind a quartz slide, backed by an ordinary glass slide to retard evaporation. When sunlight is used, ordinary thin microscope slides may be used. The degree of darkening may be evaluated by comparison with standards.

Some reversible darkening in daylight of commercial samples of titanium oxide,[112] particularly in those containing iron, has been observed to occur. Vermillion is also light-sensitive.[113]

EFFECT OF ULTRAVIOLET RADIATIONS ON COLLOIDAL SYSTEMS

Preparation. Although Schulze [114] was unable to effect the conversion of metals into dusts by the action of ultraviolet radiation, Svedberg [115] succeeded in preparing colloidal sols of metals by applying an observation of Lenard and Wolf [116] that certain substances, especially metals, are disintegrated when exposed to ultraviolet rays. Pieces of metal, the surfaces of which had been carefully freed from oxides, were placed in a shallow dish containing a dispersion medium, and exposed to the rays from a Heraeus quartz mercury arc lamp at a distance of a few centimeters. After a few minutes, colloidal sols were obtained from silver, copper, tin and lead, but platinum, aluminum and cadmium remained practically unaffected. The action was especially marked in the case of lead, which yielded a colloidal sol in ethyl alcohol, and a milky liquid, probably containing lead hydroxide, in water. The nature of the dispersion medium had a great influence on the results with silver and lead. Kimura [117] tested the effect of ultraviolet rays on silver, copper and an alloy of cadmium 90 per cent and antimony 10 per cent. In a vacuum, no corrosion took place, in air, there was a very slight corrosion, in oxygen somewhat more and in water strong corrosion under the influence of the rays. Nordenson,[118] who continued these experiments, using quantitative methods, ascribed the formation of the colloidal sols by the rays to the formation of hydrogen peroxide. This attacks the metal, yielding an oxide or hydrate which after solution is converted to a metallic colloid by the reducing action of the rays.

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[111] Gardner, H. A., and Holdt, P. C., *U. S. Paint Mfrs. Circ.*, **194**, 174 (1924); *Chem. Abs.*, **18**, 910 (1924).

[112] Williamson, W. O., *Nature*, **140**, 238 (1937); **143**, 279 (1939).

[113] Six, G., and Bover, J. R., *Paint Manuf.*, **8**, 367 (1938); *Chem. Abs.*, **33**, 883 (1939).

[114] Schulze, F., *Ber. Physik. Ges.*, **1912**, 246; *Chem. Abs.*, **6**, 1708 (1912).

[115] Svedberg, T., *Ber.*, **42**, 4375 (1909); *Z. Chem Ind. Colloide*, **6**, 129, 238 (1910).

[116] Lenard and Wolf., *Ann. Phys. Chim.*, **37**, 443 (1889).

[117] Kimura, M., *Mem. Coll. Sci. Eng. Kyoto Imp. Univ.*, **5**, 253 (1913); *Chem. Abs.*, **8**, 611 (1914).

Dede and Walther[119] obtained yellow to bluish-violet colloidal solutions of arsenic by bubbling purified arsine through water exposed to light of short wavelengths.

Voigt[120] has stated that pure silver nitrate in very dilute solution does not form a silver hydrosol when exposed to the rays from a quartz lamp except in the presence of a protective colloid such as gum arabic. The wave-length is important, ultraviolet rays being required. The ultramicroscopic particles of the gum act as reducing centers.

Wassiljewa[121] notes that if dilute hydrochloric acid is added to a solution of sodium tungstate until the liquid becomes slightly acid, a colloidal solution of tungstic acid is obtained. This, in the presence of various organic substances such as formaldehyde, sucrose, dextrose or dextrin, undergoes reduction on exposure to light, with the formation of an intensely blue solution. If the undialyzed solution is kept for some time, it is found that the reduction process does not occur when the solution is exposed to light. This may be due to the existence of two forms of colloidal tungstic acid, one of which is photochemically inert and the other sensitive to light. The latter changes spontaneously into the former. The reverse transformation may be brought about by a rise of temperature. The absorption spectra of the two modifications are found to differ appreciably, the region of ultraviolet absorption extending further towards the visible spectrum in the case of the photochemically sensitive modification. Ghosh and Bhattacharya[122] found that it takes three minutes to start the photochemical reduction of tungstic acid by glucose in the presence of sunlight. The rate of reaction then increases up to eight minutes, after which it obeys a zero-molecular law. This period of induction is probably due to the fact that the aggregated molecules must first be broken up into simple molecules before the reduction begins.

It has been claimed[123] that alumina intended for use as an emulsifying agent in the manufacture of cosmetics, paints and cleaning agents may be improved by ripening it by ultraviolet irradiation.

In determinations of particle size in colloidal sols, it has been possible to make observations of the Tyndall cone produced by ultraviolet as well as by visible light.[124, 125]

Effects of Irradiation on the Stability of Colloidal Systems. Ultraviolet rays cause a slight decrease in the electrophoretic migration velocity of zinc hydrosols, but not alcosols, according to Schaum and Friederich.[126] Light also affects the electrophoresis of silver halide hydrosols and may even reverse the direction of migration of the particles. The migrations of many other sols were not, however, affected by light in Schaum's experiments.

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[118] Nordenson, H., *Kolloidchem. Beihefte*, **7**, 110 (1915).

[119] Dede, L., and Walther, T, *Ber.*, **58B**, 99 (1925). For data on the effects of ultraviolet irradiation upon the growth of the particles of sulfur and of gum mastic sols, see Audubert, R., *Ann. Phys.*, **18**, 5 (1922); *Chem. Abs.*, **16**, 3812 (1922).

[120] Voigt, J., *Kolloid-Z.*, **43**, 30 (1927); **45**, 319 (1928).

[121] Wassiljewa, A., *Z. wiss. Phot.*, **12**, 1 (1913); *J. Chem. Soc.*, **104**, ii, 265 (1913).

[122] Ghosh, S., and Bhattacharya, A. K., *Bull. Acad. Sci. United Provinces Agra Oudh, India*, **2**, 29 (1932); *Chem. Abs.*, **27**, 2097 (1933); Ghosh, J. C., and Banerjee, T., *Kolloid-Z.*, **86**, 372 (1939).

[123] Dickerson, T. W., British P. 487,855, June 25, 1938.

[124] Lohfert, H., *Kolloid-Z.*, **51**, 65 (1930).

[125] With reference to the action of ultraviolet in producing fog nuclei, see Ramsauer, C., *Ber. deut. Physik. Ges.*, **13**, 899 (1911); *J. Chem. Soc.*, **102**, ii, 5 (1912). On the formation of nuclei in moist air, Saltmarsh, M., *Proc. Phys. Soc.*, **27**, 357 (1915).

A number of investigators have studied the effect of ultraviolet light in altering the stability of particle size of previously prepared colloidal sols. In experiments in which silver sols prepared by the high-frequency arc method were adsorbed by filter paper and exposed to the rays, Long[127] found the more highly dispersed ones to be particularly sensitive. Wiegel[128] also noted that coagulation of dextrin-silver sols is accelerated by light, and especially the shorter wave-lengths. Galecki and Spychalski[129] found that the smaller the particles of silver nuclear hydrosols, the more readily were they decolorized by ultraviolet rays. The conductivity increases and the viscosity decreases, but these changes may be reversed on prolonged irradiation. It is suggested that the radiation causes the formation of hydrogen peroxide, which dissolves the colloidal silver and decolorizes the sol by forming silver ion. This may subsequently be reduced by the action of the ultraviolet rays. The reaction, as followed by spectrophotometry at 5100A, appeared to be of the first order. The values of the reaction velocity constants varied at 10° from 0.0528 to 0.1345 and at 29° from 0 0875 to 0.2104 for the particular sols used. The temperature coefficient had a mean value of 1.3. According to Galecki and Marchlewska,[130] gelatin and ageing increase the time required for ultraviolet light to decolorize the sols.

The coagulation of Bredig's platinum hydrosol[131] may be greatly hastened by exposure to a 220-volt Cooper-Hewitt quartz lamp at a distance of 15 cm. A platinum sol which was not completely coagulated in two years in ordinary light was half coagulated in ten hours of irradiation Similarly, the rays accelerate the coagulating action of common salt.

Zakowski[132] finds the induction period or period of slow growth of gold particles upon gold nuclei to be diminished by previous irradiation of the gold solution by ultraviolet light. Beaver and Muller[133] have reviewed the many older observations regarding the effect of light in reducing gold salts or in accelerating the action of reducing agents in the formation of colloidal gold. Nordenson[134] was convinced that the coagulating effect of the ultraviolet rays upon gold sols was not due to a photoelectric effect because the result was the same for positively and for negatively charged particles. He suggested either that the light may cause a difference of potential between adjacent particles leading to attraction and eventual precipitation, or that the light may disturb the adsorption equilibrium between particles and associated ions, leading to instability and coagulation Beaver and Muller attempted to determine why the sensitivity of gold sols is markedly dependent upon their past history, some being entirely unaffected by ultraviolet light, while others are readily coagulated by it. Fourteen days' exposure to a 220-volt mercury arc did not affect Bredig gold sols or sols prepared by means of hydrazine, phosphorus, formaldehyde or acetylene. On the other hand, sols prepared by means of hydrogen peroxide, tannin, quinol, catechol, resorcinol or pyrogallol, turned blue within the first two days, the light having a slow coagulating effect. After eight days of irradiation, they turned clear red, the unstable sol being peptized to a sol identical in appearance and behavior with the one originally used. After this, light had no further effect. In the case of the tannin and hydrogen peroxide sols, the stability toward ultraviolet radiation was in general dependent upon the pH at which the reduction had originally been brought about. The sensitivity toward radiation was progressively less as neutrality was approached, and was at a minimum at slight alkalinity for the peroxide sols. In the range of pH 7.5 to 9.0, the sensitivity, although slight, varied, so that a number of the sols identical in appearance exhibited different behavior toward the light. Radiation of wave-lengths shorter than the 2150A line is required for the change from red to blue. In a tannin sol, there was a slight but definite increase of the refractive index as the sol became blue. It decreased again as the sol was peptized by the radiation. The changes were even less in a hydrogen peroxide sol. The conductivity changed in a similar manner to the extent of about 0.3 per cent. These effects were attributed to changes in the amounts of stabilizing ions adsorbed. As more ions appeared in the solution in the first part of the irradiation, fewer were adsorbed and the stability was decreased. The absorption spectrum of the sol proved one of the most sensitive indicators of the changes taking place. Conductance titrations with silver nitrate indicated an increased concentration of chloride ion in the bulk of the solution in the blue sol and a return to the original concentration in the peptized red sol. Although the original and the red final states appeared to be identical, it was evident from the photochemical indifference of the latter that they are in fact different. This was also apparent from spectrograms in the far ultraviolet, since the peptized sol no longer absorbed the effective radiation. It is possible that when peptization had been effected, the ions were more firmly associated with the complex; this would account for the greater stability toward light as well as for the lack of absorption bands in the effective region.[135]

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[126] Schaum, K., and Friederich, P., *Z wiss. Phot.*, **23**, 98 (1924); *Chem Abs*, **19**, 1376 (1925).

[127] Long, S. H., *Kolloid-Z*, **14**, 136 (1914).

[128] Wiegel, E., *Z. wiss. Phot.*, **24**, 316 (1927); *Brit Chem Abs*, **A1927**, 411

[129] Galecki, A, and Spychalski, R., *Rocsniki Chem*, **8**, 394 (1928); *Z. anorg allgem. Chem.*, **177**, 337 (1928); *Kolloid-Z.*, **53**, 338 (1930); *Chem. Abs.*, **23**, 1572 (1929); **25**, 876 (1931).

[130] Galecki, A., and Marchlewska, J., *Kolloid-Z.*, **59**, 206 (1932).

[131] Spear, E. B., Jones, P. F., Neave, A. S., and Schlager, M, *J. Am. Chem Soc*, **43**, 1385 (1921).

[132] Zakowski, J., *Kolloidchem. Beihefte*, **23**, 117 (1926).

[133] Beaver, J. J., and Muller, R. H., *J. Am. Chem. Soc*, **50**, 304 (1928).

[134] Nordenson, H., *Z. physik. Chem.*, **90**, 603 (1915).

It has been shown by Murphy and Mathews [136] that the electrical conductivity of arsenic trisulfide hydrosol increases upon exposure to light, the rate of change increasing somewhat with decreasing concentration of the colloid.

According to Freundlich and Moor,[137] a mixture of silver and arsenious sulfide sols undergoes in the dark a change of color from a golden-brown through greenish-brown to lilac, and, with exposure to light, through green to a golden-brown. Both changes are prevented in the presence of a gelatin gel. The reaction in the dark is regarded as a direct interaction between the particles of the two sols. The secondary change under the action of light is purely chemical and involves oxygen and the probable formation of a silver thioarsenite. Horiba and Baba [138] find that on illumination, arsenious sulfide and Congo red sols, but not ferric or chromic hydroxide sols, exhibit increased osmotic pressure. Colloidal cuprous hydroxide, formed by boiling cuprous chloride or bromide with aqueous gelatin, is photosensitive in the presence of acid.[139]

The reactions of gold and silver sols with arsenic and antimony trisulfide sols are photosensitive.[140] Rapid color change is produced by sunlight and the product is found to consist of metallic sulfides, free sulfur and arsenious or antimonious acids.

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[135] See also Thiessen, P. A., *Kolloidchem. Beihefte*, **29**, 122 (1929).

[136] Murphy, R. V., and Mathews, J. H., *J. Am. Chem. Soc.*, **45**, 16 (1923).

[137] Freundlich, H., and Moor, F., *Kolloid-Z.*, **36**, 17 (1921).

[138] Horiba, S., and Baba, H., *J. Phys. Chem. Japan*, **3**, 1 (1929); *Brit. Chem. Abs.*, **A1930**, 691.

[139] Horiba, S., and Ishii, S., *J. Phys. Chem. Japan*, **2**, 118 (1929); *Brit. Chem. Abs.*, **A1930**, 691.

Krestinskaya[141] found arsenious sulfide sols to be rendered more stable toward the barium ion by exposure to light. Sols of different concentrations and compositions were, however, affected differently in respect to the coagulating action of other ions. According to Joshi, Barve and Desai,[142] on exposure of an arsenious sulfide sol to light, the charge on the particles decreases, the conductivity increases, the total sulfur decreases, the stability to potassium chloride passes through a maximum, and the stability to magnesium chloride decreases continuously. These effects are attributed to the hydrolysis of the sulfide to arsenious acid and hydrogen sulfide, the latter yielding sulfur dioxide, sulfur and pentathionic acid.

Boutaric and Bouchard[143] found the time of coagulation of arsenious sulfide and other sols by electrolytes in the presence of fluorescein, eosin or erythrosin, was in all cases decreased by illumination, the effect being greater in ultraviolet than in visible light freed from infrared. Potassium sulfate and sulfuric acid, which inhibit the fluorescence of the dyes, also suppress the effect of the light. The light had no effect in the absence of the fluorescent compounds, and the dyes did not affect the sols in the dark. The difference between the time required for flocculation in the dark and in daylight or ultraviolet light is proportional to the logarithm of the fluorescing power of the mixture of fluorescein and added electrolyte, if any. Tannin, hydroquinone, phenol and cresol in the presence of lithium chloride also reduce both the fluorescing power and the shortening of the flocculation time. Eosin and erythrosin which have absorption bands close to that of fluorescein, reduce its fluorescence and also reduce its effect on the flocculation time. The difference in the time required for flocculation in the dark and in ultraviolet light is reduced from 60 to 15 minutes by 0.05 per cent Direct-Scarlet solution. A number of colorless substances which fluoresce in the ultraviolet were also found effective. Among these are esculin and a number of naphtholsulfonic acids.

X-rays, ultraviolet radiations and α-rays cause the coagulation of sols of cerium hydroxide and albumin, and the inversion of cane sugar solutions, according to Fernau.[144]

Berlin blue hydrosols are decolorized and coagulated by visible and ultraviolet light. The time of flocculation by irradiation is proportional to the layer thickness and sol concentration; the optimum wave-length is 4200A.[145] Lal and Ganguly[146] found, however, that Prussian blue and gum mastic sols were not coagulated by the full radiation of the quartz mercury arc, although various sulfide sols (arsenic, cadmium, antimony, and ferrous), metallic sols (platinum, silver and gold), sulfur sols, hydroxides (cerium, thorium, ferric) were affected. The pH of the sols varied during exposure, some increasing and some decreasing. Coagulation was attributed to the destruction of stabilizing agents by the action of the light. These observations were extended by Miss Roy.[147] Sols of stannic, aluminum and thorium hydroxides, of antimony, arsenious and mercuric sulfides, acquired increased conductivity after exposure, although uranium and cupric ferrocyanide sols did not. She found a short exposure to increase the stability of arsenious and antimony sulfides and uranium and cupric ferrocyanides, but on longer exposure all became less stable, and sols of antimony sulfide, mercuric sulfide and uranium ferrocyanide coagulated completely.

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[140] Bhatnagar, S. S., Yajnik, N. A., and Zadoo, V. D., *Quart. J. Indian Chem. Soc.*, **4**, 209 (1927); *Chem. Abs.*, **21**, 3514 (1927).

[141] Krestinskaya, V., *Kolloid-Z.*, **66**, 58 (1934); *Chem. Abs.*, **28**, 1909 (1934).

[142] Joshi, C. B., Barve, P. M., and Desai, B. N., *Current Sci.*, **3**, 105 (1934); *Chem. Abs.*, **29**, 22 (1935).

[143] Boutaric, A., and Bouchard, J., *Compt. rend.*, **192**, 95, 357 (1931); **193**, 45 (1931); **194**, 1245 (1932); *Bull. Soc. Chim.*, **51**, 757 (1932); Pospelov, A., and Pospelova, K., *J. Phys. Chem. (U.S.S.R.)*, **5**, 52 (1934); *Chem Abs.*, **28**, 4315 (1934).

[144] Fernau, A., Kolloid-Z., **33**, 89 (1923); Chem. *Abs.*, **17**, 3837 (1923).

[145] Lederer, E. L., and Hartleb, O., Kolloid-Z., **62**, 42 (1933); Chem. *Abs.*, **27**, 1800 (1933).

[146] Lal, P., and Ganguly, P. B., *J. Indian Chem. Soc.*, **6**, 547 (1929); *Chem. Abs.*, **24**, 540 (1930).

[147] Roy, S., *J. Indian Chem. Soc.*, **6**, 431 (1929); *Chem. Abs.*, **23**, 4865 (1929).

Heller[148] has considered the case in which the photochemical action is on the adsorbed electrolyte; coagulation is then probably due to the critical diminution of the double layer and the effect of light should be expected to be greater as the double layer is initially weaker. Sols of ferric oxide obtained by hydrolysis of ferric nitrate were dialyzed for three to twenty-five days and examined magneto-optically after varying periods in darkness followed by exposure to diffused light. The rate of growth of size of particles decreased with the time in darkness, but increased again on exposure to light, the increase being greatest in the sols longest dialyzed and so least stable.

Emulsions of benzene, benzine and carbon disulfide in water with sodium oleate as the emulsifier separated into two layers when irradiated with ultraviolet light.[149] The pH of the illuminated emulsion increased, indicating that its breaking was due to the partial destruction of the emulsifying agent.

Effects of Irradiation on Liesegang Ring Formation. Light of short wave-length is reported by Davies[150] to aid in the production of colored bands of colloidal gold in silicic acid gels containing gold chloride and various reducing agents. The work was extended by Cadenhead[151] to include the effects of x-rays. Both workers agree that the banding on reduction to colloidal gold is not a true Liesegang phenomenon. It has been observed[152] that the passage of a beam of light through soil or kaolin suspensions contained in a rectangular tank causes the suspensions to stratify, the layers running parallel to the surface. The distance between the successive strata appears to vary with the wave-length of the light, but the strata produced by white light are quite sharp. The stratification persists while the illumination is continued, and slowly disappears when it is cut off.

Blair[153] points out that in gels in either intense white light or complete darkness there is irregular Liesegang ring formation, which persists even after liquefaction and resetting. Ultraviolet rays from a quartz mercury lamp in a few hours render a gel incapable of Liesegang ring formation, but this effect does not persist after liquefaction.

Ultraviolet radiations cause a marked disturbance[154] in the rings formed round a drop of silver nitrate solution placed on a film of setting gelatin. X-rays and radium have no effect. The radiation restrains the primary rings and prevents the formation of secondary ones.[155] In the case of silver chromate-gelatin,[156] visible light causes the number of bands to increase and the distance between them to shorten. Ultraviolet rays retard the formation of rings, which are finer and closer together than in the dark. Nikiforov and Lemeche[157] believe the "pressure" of Liesegang rings directly proportional to the light intensity. The number of rings per unit of distance increases under both ultraviolet and diffused daylight. Similar observations have been recorded by Miyamoto.[158] Chloride ions in definite concentrations seem to be necessary for light to have an effect on the production of the rings.[159]

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[148] Heller, W., *Compt. rend.*, **199**, 723 (1934).

[149] Sinha, P. C., and Ganguli, P. B., *Kolloid-Z.*, **54**, 147 (1931).

[150] Davies, E. C. H., *J. Am. Chem. Soc.*, **45**, 2261 (1923).

[151] Cadenhead, A. F. G., *Can. Chem. Met.*, **10**, 201 (1926); *Chem. Abs.*, **20**, 3390 (1926).

[152] Morrison, C. G. T., *Proc. Roy. Soc. London*, **108A**, 280 (1925).

[153] Blair, G. W. S., *Phil. Mag.*, **49**, 90 (1925).

[154] Cluzet, J., and Kofman, T., *Compt. rend. soc. biol.*, **104**, 1001 (1930); *Chem. Abs.*, **25**, 3245 (1931); see also Hatschek, E., *Kolloid-Z.*, **37**, 297 (1925); *Proc. Roy. Soc. London*, **96A**, 496 (1921) for similar observations on lead chromate bands.

[155] Kofman, T., *J. chim. phys.*, **29**, 586 (1932); *Compt. rend., 208, 567 (1939).*

[156] Isemura, T., *Bull. Chem. Soc. Japan*, **8**, 108 (1933); *Chem. Abs.*, **27**, 4152 (1933); Taboury, M.-F., and Bellot, M., *Compt. rend.*, **205**, 45 (1937). See also Teft, R., and Hill, J. W., *Trans. Kansas Acad. Sci.*, **33**, 57 (1931) for some effects of light on the formation of banded precipitates of mercuric iodide.

It is held by Alekseevskii[160] that the adsorptive power of active charcoal and of silica gel is increased by irradiation with ultraviolet rays.

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[157] Nikiforov, V.-K., *J. chim. phys.*, **32**, 585 (1935). Nikiforov, V.-K., and Lemèche, M.-R., *Ibid.*, **33**, 250 (1936)

[158] Miyamoto, S., *Kolloid-Z.*, **78**, 23 (1937).

[159] Köhn, M., and Mainzhausen, L., *Kolloid-Z.*, **79**, 316 (1937)

[160] Alekseevskii, E. V., *J. Russ. Phys.-Chem. Soc.*, **60**, 1173 (1928); *Chem Abs*, **23**, 2367 (1929).

Chapter 22

The Reactions of Organic Compounds. Aliphatic Series[1]

A very considerable body of empirical information has been accumulated regarding the photochemical behavior of a wide range of organic compounds, in large part due to the pioneering observations of Ciamician and Silber on the effects of prolonged exposures to sunlight and of Berthelot and Gaudechon on the effects of ultraviolet light. Unsaturated hydrocarbons rayed with ultraviolet undergo stereoisomeric transformations or polymerize. Alcohols, aldehydes and ketones decompose into carbon monoxide, hydrogen and hydrocarbons under some conditions. Acids may yield carbon dioxide and a hydrocarbon, with some carbon monoxide and hydrogen. Dibasic acids readily lose carbon dioxide, leaving monobasic acids. Keto acids react in ultraviolet when heated.

The theoretical interpretations of this behavior and its relation to the absorption spectra of the compounds studied has been most advanced in the case of the aldehydes and of the interconversions of geometrical isomers.

SATURATED HYDROCARBONS

The ultraviolet absorption spectra of the saturated hydrocarbons lies in the extreme ultraviolet. This accounts for the observed inertness of these compounds to the ordinarily available ultraviolet radiations.[2]

Methane is unaffected by the radiations between 2300 and 4000A.[3] With a Harteck xenon lamp giving 3×10^{16} quanta per second, the 1469A line is 13 per cent and the 1295A line 100 per cent absorbed by a 30-mm. layer of the gas at atmospheric pressure.[4]

The methane is decomposed in the primary process into methyl radicals and hydrogen atoms, the final products being hydrogen and acetylene, traces of ethylene, ethane and hydrocarbons with three to five carbon atoms.

Leighton and Steiner[5] also state that the radiation from a hydrogen discharge tube transmitted by a thin fluorite window decomposes methane with a quantum yield of the order of unity. They identified hydrogen and possibly ethylene in the approximate molecular ratio of four to one.

According to Tolloczko,[6] ethane irradiated in quartz with rays of wave-lengths between 2300 and 4000A gave a small amount of a light colorless condensate, composed of a mixture of hydrocarbons, mostly hexane; the gas contained hydrogen and methane. Klemenc and Patat[7] claim that pentane suffers decomposition and polymerization. The polymerization products take up oxygen, breaking the carbon chain and producing methane and carbon monoxide and dioxide.

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[1] For a general review, see Bonhoeffer, K. F., *Z. Elektrochem*, **40,** 425 (1934).

[2] Glockler, G., *Proc. Nat Acad Sci*, **11,** 74 (1925); Kemula, W., and Mrazek, S, [*Compt. rend.*, **195,** 1004 (1932)] found methane, ethane and butane not to absorb between 6000 and 1965A.

[3] Tolloczko, S., *Przemysl Chem.*, **11,** 245 (1927); *Chem. Abs.*, **22,** 4380 (1928).

[4] Groth, W., and Laudenklaus, H., *Naturwiss*, **24,** 796 (1936); Groth, W., *Z. physik. Chem.*, **B38,** 366 (1937); see also Kemula, W., and Dyduszynski, A., *Roczniki Chem.*, **17,** 423 (1937); *Brit. Chem. Abs.* **A,** 39 (1938).

[5] Leighton, P. A., and Steiner, A. B., *J. Am. Chem. Soc.*, **58,** 1823 (1936).

[6] Tolloczko, S., *loc. cit.*

Because of their transparency to ultraviolet rays, the liquid hydrocarbons are especially suitable solvents for use in measuring the absorption spectra of various organic solutes. Castille and Henri[8] have given detailed directions for the purification of hexane for this purpose. Samples of hexane prepared by their methods transmitted, in 40-mm. layers, to 1900A. Butane prepared by the Grignard method may contain an unidentified substance which shows fifteen absorption bands between 2206 and 1965A.[9] This impurity can be removed by long agitation with bromine water. In the Schumann regions, heptane and hexane have an absorption maximum at 1500A.[10] In the unsaturated compounds 1-heptylene, 2-pentylene, 1-pentylene, trimethylethylene, this is shifted to 1750A. These bands are without fine structure and are attributed to the dissociation of a carbon-carbon bond. Duncan and Howe[11] state that methane shows true continuous absorption in the region between 1450 and 850A, such continuous spectra being general for molecules with tetrahedral symmetry.

Mercury-sensitized reactions of ethane have recently been described by Kemula, Mrazek and Tolloczko.[12] Butane, hexane and octane are formed together with traces of methane. The proportion of butane in the product varies directly with the rate of flow and the pressure of the ethane, and inversely with the temperature of the receiver. Both the carbon-carbon and carbon-hydrogen linkings are affected. When butane is removed by a low-temperature trap, the reaction products, according to Steacie and Phillips, are exclusively methane, propane and butane. The quantum yield for ethane decomposed is 0.2.[13]

Taylor, Morikaw and Benedict[14] found that methane reacts with deuterium at 40° to 300°C. in the presence of mercury vapor excited by its resonance radiation The degree to which the substitution occurs depends upon the time and temperature of irradiation. Farkas and Melville[15] proposed a chain mechanism for the reaction at temperatures over 300°C.:

$$\begin{aligned} D + XH &\longrightarrow DX + H \\ H + D_2 &\longrightarrow HD + D. \end{aligned}$$

The oxidation of methane, methyl chloride and methylene chloride may be sensitized to light of the wave-length 4360A by chlorine.[16] The products from each of these compounds include carbon monoxide and hydrogen chloride, as well as small amounts of water, phosgene and several heavy volatile organic compounds. The quantum yield varies from 80 for methane to 800 for methylene chloride.

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[7] Klemenc, A., and Patat, F., *Z. physik Chem.*, **149A**, 449 (1930); see also Landau, M., *Compt. rend.*, **155**, 403 (1912); *J. Chem. Soc.*, **102**, II, 986 (1912).

[8] Castille, A, and Henri, V., *Bull. Soc. chim. biol.*, **6**, 299 (1924); the observations of Urbain, E, and Scal, C., [*Compt. rend.*, **168**, 887 (1919)] on the decomposition of saturated liquid hydrocarbons by ultraviolet rays may have been due to the presence of impurities.

[9] Kemula, W., and Mrazek, S, *loc. cit.*

[10] Carr, E. P., and Stücklen, H., *Helv. Phys. Acta*, **6**, 261 (1933).

[11] Duncan, A. B. F., and Howe, J. P., *J. Chem. Physics*, **2**, 851 (1934).

[12] Kemula, W., Mrazek, S., and Tolloczko, S., *Chem. Listy*, **26**, 466 (1932); *Chem. Abs*, **27**, 3142 (1932).

[13] Steacie, E. W. R., and Phillips, N. W F., *J. Chem. Phys*, **6**, 179 (1938).

[14] Taylor, H. S., Morikaw, K., and Benedict, W. S., *J. Am. Chem. Soc.*, **57**, 383 (1935); *J. Chem. Phys.*, **5**, 212 (1937).

[15] Farkas, A., and Melville, H. W., *Proc. Roy. Soc.*, **157A**, 625 (1936).

[16] Brenschede, W., and Schumacher, H. J, *Z. physik. Chem.*, **177A**, 245 (1936).

These are all chain reactions, involving the formation of intermediate, short-lived peroxides. Methane and methyl chloride also suffer chlorination to methylene chloride, some molecules of which on colliding with chlorine atoms form the $CHCl_2$ radical. This, reacting with oxygen, goes through various intermediate compounds to carbon monoxide and hydrogen chloride. The reactions of methane and methyl chloride, but not that of methylene chloride, are inhibited by an excess of oxygen.[17]

Cyclopropane undergoes a mercury-sensitized photochemical polymerization to a colorless oil of high boiling point under the influence of the resonance line of mercury.[18] The I. G. Farbenindustrie A.-G [19] claims the conversion of cyclohexanone into caproic acid by irradiation.

ALKYL HALIDES

Absorption Data. The absorption of methane is gradually shifted to longer wave-lengths as the number of halogen atoms introduced is increased.[20] However, most alkyl halides absorb but slightly. The bromides absorb more and at longer wave-lengths than the chlorides, methyl bromide absorbing nearly as well as carbon tetrachloride. The foot of the absorption curve of carbon tetrabromide approaches the visible spectrum. The iodine compounds absorb still more readily, iodoform absorbing in the visible portion of the spectrum.

Herzberg and Scheibe [21] found methyl iodide, bromide and chloride to show continuous absorption bands, with maxima at 2500, 2000, and 1750A, attributed to dissociation of the molecule into the methyl group and a halogen atom, one of the products being in an excited state. Iredale and Mills [22] found the energies of the carbon-to-iodine and carbon-to-bromine linkings, as calculated from the long wave-length limits of the continuous bands, to be in good agreement with the values calculated from the heats of combustion.[23]

Hukumoto,[24] who made similar calculations, reported data on the continuous absorption spectra of about forty alkyl halides. The iodides exhibited two or three absorption regions, the one with longest wave-lengths corresponding to a decomposition into a normal alkyl radical and an iodine atom in the metastable $2^2P_{1/2}$ state. The excess energy in the second and third continuous absorption regions was thought to be associated with excitation of the alkyl radicals.

Parti and Samuel [25] interpret the absorption spectrum of methyl iodide as involving a simultaneous loss of a hydrogen and an iodine atom. They pointed out that the beginnings of the first selective absorption of twelve alkyl halides agree with the estimated energy differences $D(CX_4)-D(CX_2)$. This viewpoint, based on an analogy with the behavior of the tin halides, appears to involve a consid erable revision of the current theories of the photochemical processes in which the alkyl halides participate.

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[17] Schumacher, H. J., *Z. Elektrochem.*, **42**, 522 (1936).

[18] Harris, L., Ashdown, A. A., and Armstrong, R. T., *J. Am. Chem. Soc.*, **58**, 852 (1936).

[19] I. G. Farbenindustrie A.-G, British P. 314,267, 1928.

[20] Lowry, T. M., and Sass, R. B., *J. Chem. Soc.*, 622, 1926.

[21] Herzberg, G., and Scheibe, G., *Trans Faraday Soc.*, **25**, 716 (1929), *Z. physik. Chem.*, **7B**, 390 (1930).

[22] Iredale, T., and Mills, A. G., *Proc. Roy. Soc.*, **133A**, 430 (1931). See also *Z. physik. Chem.*, **20B**, 340 (1933).

[23] For details of the calculation of the heats of dissociation of the carbon-halogen bond by this method, see also Sen-Gupta, P. K., *Bull. acad. Sci. United Provinces Agra Oudh, India*, **2**, 115 (1933); *Chem. Abs.*, **27**, 3668 (1933).

[24] Hukumoto, Y., *Phys. Rev.*, **42**, 313 (1932); *Science Repts. Tohoku Imp. Univ. First Ser.*, **22**, 13 (1933); **21**, 906 (1932). Data on methyl bromide are given by Fink, P., and Goodeve, C. F., *Proc. Roy. Soc.*, **A163**, 592 (1937).

[25] Parti, Y., and Samuel, R., *Current Sci.*, **5**, 386 (1937); *Chem. Abs.*, **31**, 3385 (1937); Bergmann, E., and Samuel, R., *Nature*, **141**, 832 (1938).

As determined by Saha,[26] who obtained the limit of continuous absorption from spectrograms by the method of Herzberg and Scheibe, the wave-length limits and their values in kcal. for the C—Cl bond are in carbon tetrachloride, 2800A, 102, in chloroform, 2660A, 107.5, and in methylene chloride, 2500A, 114.4 kcal. These results are considered as in good agreement with those calculated thermochemically, if allowance be made for uncertainty as to the energy state of the carbon atom.[27]

The alkyl halides also exhibit discontinuous absorption beginning at 2010, 1785 and 1600A for methyl iodide, bromide and chloride, respectively, according to Herzberg and Scheibe.[28] The discontinuous bands are considered to indicate transitions into several excited electronic states.[29]

Reactions. Although early observers made frequent reference to the decomposition of alkyl halides in light,[30] Stobbe and Schmitt [31] showed that the effects noted in daylight were due to an oxidation. In the absence of oxygen the halides are relatively light-stable. They did, however, show that a photochemical liberation of bromine from ethyl bromide occurs in the short wave length ultraviolet to a slight extent. Similar reactions occur also with the iodides, isopropyl iodide being less stable than either *n*-propyl, ethyl or methyl iodides.

The products formed when ethyl iodide is photochemically decomposed in the absence of oxygen include, according to Emschwiller and Job,[32] besides iodine, a gas composed principally of ethylene and ethane, with smaller amounts of butane and hydrogen. The formation of the butane could be explained as due to a combination of two ethyl radicals liberated in the primary process. The ethylene and ethane were accounted for by assuming that the primary process for the most part consists in a simultaneous loss of both hydrogen and iodine atoms from the ethyl iodide as hydrogen iodide, leaving ethylene. (The ethane might then arise by combination of ethylene with hydrogen produced by the photodecomposition of the hydrogen iodide.[33]) In similar fashion, propyl iodide yielded propylene and propane, normal, secondary and isobutyl iodides gave butylene and butane, and methyl iodide gave methane Tertiary butyl iodide gave propylene and propane, ethylene and ethane. In these experiments the alkyl halides were irradiated as liquids. Emschwiller believed both the hydrogen and the iodine atoms to be liberated from the same carbon atom, the residue rearranging to give the olefine. He also believed studies of the photochemical oxidation of the alkyl halides to corroborate this conception, methyl iodide, ethyl iodide and isopropyl iodide giving formaldehyde, acetaldehyde and acetone, respectively.[34] It may be noted that Emschwiller's conception of the primary process is in agreement with that of Parti and Samuel, although the latter workers do not postulate a rearrangement of the radical with divalent carbon to an olefin.

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[26] Saha, N. K., *Bull. Acad. Sci. United Provinces Agra Oudh, India*, **2**, 233 (1933); *Chem. Abs.*, **27**, 4733 (1933). For further data on other halides, see Rehman, R A, Samuel, R, and Sharf-ud-Din, *Indian J. Physics*, **8**, 537 (1934); Price, W. C., *Phys. Rev*, **47**, 419 (1935), *J. Chem. Physics*, **3**, 365 (1935); **4**, 547 (1936)

[27] For the absorption spectra of more complex halides, see Fukumoto, Y, *Science Repts., Tokoku Imp. Univ. First Series*, **23**, 62 (1934).

[28] Also Scheibe, G., Povenz, F., and Lindström, C. F., *Z. physik. Chem.*, **20B**, 283 (1933).

[29] See also Henrici, A., *Z. Physik*, **77**, 35 (1932) and for the theoretical interpretation of the methyl iodide bands, Mulliken, R. S., *Phys. Rev*, **47**, 413 (1935), and Porret, D, and Goodeve, C. F., *Trans. Faraday Soc.*, **33**, 690 (1937); *Proc. Roy. Soc.*, **A165**, 31 (1938).

[30] Schoorl, N., and Van den Berg, L. M., *Pharm. Weekblad*, **43**, 218 (1906); Benrath, A., *Annalen*, **382**, 222 (1911).

[31] Stobbe, H., and Schmitt, P., *Z. wiss. Phot.*, **20**, 57 (1920).

[32] Emschwiller, G., and Job, A., *Compt. rend*, **179**, 52, 168 (1924).

[33] Emschwiller, G., and Job, A., *Compt. rend.*, **192**, 799 (1931); **193**, 1003 (1931).

[34] Emschwiller, G., and Job, A., *Ann. Chim.*, **17**, 413 (1932).

On the other hand, Bates and Spence[35] believe the primary process, at least, in the case of gaseous methyl iodide, to consist solely in a simple dissociation into a free methyl radical and an iodine atom.[36] They also support this by a study of the reaction occurring in the presence of oxygen. In this case the methyl radical may react with oxygen to produce formaldehyde and an hydroxyl radical. The latter, on reaction with a fresh methyl iodide molecule yields methanol and an iodine atom. Methanol (two molecules) and formaldehyde may then react to produce methylal, $(CH_3O)_2CH_2$, and water. Furthermore, Spence and Wild[37] found the irradiation of pure methyl iodide in the absence of oxygen to yield no hydrogen iodide. Small amounts of methane, ethane and iodine were formed.[38] The presence of free methyl radicals in the photochemical decomposition of methyl iodide vapors has been recently demonstrated by the ortho-para hydrogen conversion test for the presence of paramagnetic substances.[39]

In his earlier work, Emschwiller[40] believed that a critical threshold wave-length for the ethyl iodide and methyl iodide decompositions had been observed at 4100A. In later observations, however, he gave up the concept of the existence of a threshold value since he had found the absorption curve of ethyl iodide to vary with the temperature, being shifted toward the visible by about 12A per 10°C.[41]

The quantum yields obtainable under various conditions have been a matter of controversy. Bates and Spence[42] found that methyl iodide vapors, when irradiated in the continuum, gave the very low quantum yield of 0.02. It was slightly greater (0.05) in hexane solution. Spence and Wild[43] put the yield of methane from methyl iodide vapor at 0.032, that of free iodine being half as great. Calculated as methyl iodide destroyed, the quantum yield is at least 0.06. Higher iodides are probably formed. The reaction is not affected by the addition of hydrogen or nitrous oxide.

Very similar results have been recorded for ethyl iodide, although Emschwiller gave yields at high temperatures for ethyl iodide seventeen or more times as great as for methyl iodide. Norton[44] found for liquid ethyl iodide the values 0.315 at 3130A, 0.38 at 2654A and 0.41 at 2537A. The higher yields of about unity reported by Iredale were believed to have been due to the presence of some oxygen.[45]

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[35] Bates, J. R, and Spence, R., *J. Am. Chem. Soc.*, **53**, 381, 1689 (1931), *Trans. Faraday Soc*, **27**, 468 (1931).

[36] A general discussion of free radicals in organic photoprocesses is due to H. S. Taylor, *J. Phys. Chem.*, **42**, 763 (1938).

[37] Spence, R., and Wild, W., *Proc. Leeds Phil. Lit. Soc., Sci. Section*, **3**, 141 (1936), *Chem. Abs.*, **30**, 2849 (1936). In the presence of hydrogen iodide, methyl iodide yields iodine with a quantum yield of two, according to Iredale, T., and Stephan, D., *Trans. Faraday Soc.*, **33**, 800 (1937).

[38] Jones, L. T., and Bates, J. R., [*J. Am Chem. Soc.*, **56**, 2285 (1934)] found the kinetics of the rapid photoöxidation of ethyl iodide to differ from that of methyl iodide. Acetaldehyde and ethanol were produced. A mechanism involving the intermediary formation of ethyl peroxide was proposed, but the observation of small deviations in the rates from those expected suggested the reaction to be one of great complexity.

[39] West, W., *J. Am. Chem. Soc.*, **57**, 1931 (1935). It also is found in the acetone decomposition, but negative tests were obtained in the irradiation of benzene and of propionaldehyde vapors.

[40] Job, A., and Emschwiller, G., *Compt. rend.*, **179**, 52,168 (1924).

[41] Job, A., and Emschwiller, G., *Compt. rend.*, **190**, 741,866 (1930); *Ann. Chim.*, **17**, 413 (1932).

[42] Bates, J. R., and Spence, R., *J. Am. Chem. Soc.*, **53**, 1689 (1931).

[43] Spence, R., and Wild, W, *Proc. Leeds Phil. Lit. Soc., Sci. Section* **3**, 141 (1936); *Chem. Abs.*, **30**, 2849 (1936).

[44] Norton, B. M., *J. Am. Chem Soc*, **56**, 2294 (1934).

[45] Iredale, T., *J. Phys. Chem.* **33**, 290 (1929). It must be noted, however, that Gibson, K. E., and Iredale, T. [*Trans. Faraday Soc.*, **32**, 571 (1936)] have found a value of unity for benzene solutions of methyl iodine in the absence of oxygen in recent redeterminations. The same value was given by γ-butyl iodide. In alcohol, methyl iodide gave values greater than one. Furthermore, iodoform in benzene gave a value of one in the absence of oxygen and higher in its presence. In alcohol, the yields seemed higher.

West and Paul[46] found the quantum yields in hexane to be a constitutive property of the alkyl group,[47] varying from a few hundredths in the case of methyl iodide to slightly over one for isopropyl iodide for the wave-length 2610A.[47a] The yield increases somewhat with decreasing wave-lengths between 3130 and 2610A, the ratios differing, however, for each of five iodides studied. They concluded a direct recombination of the iodine atom and the free radical to be the cause of the low yield for methyl iodide. (The non-dependence of the yield on the concentration made it seem that the reaction $CH_3 + CH_3I \rightarrow C_2H_6 + I$ is uncommon. Similarly, the reaction between an iodine molecule and a free methyl radical was thought to be infrequent because of the zero order of the reaction in its early stages.) Accordingly, it was suggested that the values of the quantum yields shown by the various halides might give directly the relative probabilities of recombination of the various alkyl radicals with atomic iodine. If this be admitted, the order of reactivity of the alkyl radicals would be methyl > allyl > vinyl > ethyl > propyl > isopropyl.

West and Ginsburg[48] found that, although in the pure liquid state or in hexane solution, ethyl iodide decomposes with a quantum yield of 0.6, in the vapor state the quantum yields at 2600A in the continuum are very low.

They also made observations of the quantum yields at the beginning of the short wave-length region of banded absorption at 2026A. In the vapor at 45 or 90 mm. pressure at 30°C., the yield was 0.1. At 0.1 mm. it was definitely lower, and was also lower than that of the reaction produced by this wave-length in condensed phases, the yield in the liquid being about 0.24. In the short wave-length region, interaction between excited molecules and normal molecules seemed the predominant mechanism.

Especial attention was paid, by West and Schlessinger,[49] to the products other than iodine. They found that at 2537A methyl iodide yields mostly methane and small quantities of ethylene and ethane, and that more than a third of the iodide decomposed appears as methylene iodide. Addition of silver foil increases the rate of reaction about fortyfold, yields all the iodine as silver iodide, and causes the gaseous products to consist mostly of ethane with some ethylene but much less methane than in the absence of silver. Ethyl iodide at 2537A gives ethane and ethylene in comparable proportions. At 2026A, small amounts of methane and hydrogen are also formed. Silver increases the reaction rate but does not affect the nature of the products. Inert gas up to 40 atmospheres increases the iodine yield linearly with the density of inert gas to values approaching one-third the yield in inert liquid solvents. The primary process forms iodine atoms and alkyl radicals. Recombination of these, which may occur as a bimolecular process, is the most rapid secondary process and accounts for the low quantum yields. Most of the net change is due to the reaction:

$$R' + R''H_2I \longrightarrow R'H + R''HI$$

This predominates over the association of R to R_2 and I to I_2. The quantum yield of *n*-propyl iodide vapor at 2026A is lower than that of ethyl iodide; the yields for isopropyl iodide at 2610 and 2026A are 0.17 and 0.43, respectively.

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[46] West, W., and Paul, B., *Trans. Faraday Soc.*, **28**, 688 (1932).

[47] Note also Burke, K. A., and Donnan, F. G., *J. Chem. Soc.*, **85**, 574 (1904).

[47a] Norton also notes that the quantum yield increases in various alkyl halides as the chain is lengthened, as the central carbon atom is altered from primary to tertiary and as halogen atoms are progressively introduced.

[48] West, W., and Ginsburg, E., *J. Am. Chem. Soc.*, **56**, 2626 (1934).

[49] West, W., and Schlessinger, L., *J. Am. Chem. Soc.*, **60**, 961 (1938).

According to Maynard,[50] the direct union of metallic mercury and methyl iodide is not hastened by ultraviolet rays but is accelerated by a specially arranged arc light. The reaction is preceded by the formation of a small amount of mercurous iodide. If the latter is irradiated together with methyl iodide, methyl mercuric iodide is formed rapidly. Although the action of metallic mercury is not encountered in the case of the other alkyl halides, the use of mercurous iodide makes possible the extension of the reaction to higher iodides and even to benzyl iodide.

Ramart-Lucas and Salmon-Legagneur[51] find ultraviolet light capable of converting isobutyl bromide into *tert*-butyl bromide, and propyl bromide into isopropyl bromide without any trace of dissociation occurring.

Irradiation of the vapor of methylene iodide and oxygen by the quartz mercury arc yields such products as carbon monoxide, hydrogen, iodine, formaldehyde, formic acid and ethylene glycol. The quantum yield with respect to iodine is 1.45 for light of wave-length 3100A. Gregory and Style[52] suggest CH_2, CH_2O_2 and $(CH_2O)_2$ as intermediates, the two latter substances changing into formic acid and formaldehyde, respectively. Emschwiller[53] finds iodine pentoxide to be formed particularly while some of the methylene iodide remains unattacked; it may result through the intermediary formation of peroxides of formaldehyde, formic acid, or possibly of methylene iodide.

According to Kaufmann,[54] *trans-* and *cis-α,β*-diiodoethylene and *α,α'*-diiodoethylene are decomposed with liberation of iodine when their ether solutions are exposed to ultraviolet, the velocity of the reaction in the first being approximately twice as great as that in the other two cases.

Solutions of ethylene iodide in carbon tetrachloride begin to absorb at 3600A, the absorption increasing at shorter wave-lengths. DeRight and Wiig[55] found the rate of the direct decomposition due to the absorption of the wave-lengths 3130 and 3030A approximately proportional to the absorbed energy. It increased slightly with increasing concentrations of the ethylene iodide, reached a definite maximum after the attainment of a certain amount of decomposition, and was reduced by the addition of iodine. The primary decomposition was assumed to yield atomic iodine and C_2H_4I. The quantum yield was 0.76 and the temperature coefficient 1.05. Emschwiller[56] observed[57] that vinyl iodide, irradiated 124 hours by a mercury vapor lamp, gave acetylene, ethylene and iodine and, in the presence of oxygen, also formed droplets of liquid containing formic acid, formaldehyde and $CH_2OH{\cdot}CHO$. He suggested a different mechanism for the decomposition of asymmetrical ethylene diiodide:

$$2CH_2 = CI_2 \longrightarrow C_2H_2 + C_2I_2 + 2HI.$$

$$CH_2 = CI_2 + HI \longrightarrow CH_3CI_3.$$

He also found that although $CHI = CHI$ is not oxidized in ultraviolet light, its asymmetrical isomer is completely oxidized with the formation of formic acid, a trace of formaldehyde, iodine and a gas composed of 57 per cent carbon monoxide, 23 per cent carbon dioxide and 20 per cent acetylene.

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[50] Maynard, J. L., *Science*, **56**, 492 (1922).

[51] Ramart-Lucas, Mme., and Salmon-Legagneur, F., *Compt. rend.*, **186**, 39 (1928); see also Emschwiller, G., *Ann. Chim.*, **17**, 413 (1932).

[52] Gregory, R. A., and Style, D. W. G., *Trans. Faraday Soc.*, **32**, 724 (1936).

[53] Emschwiller, G., *Compt. rend*, **206**, 746 (1938).

[54] Kaufmann, H. P., *Ber.*, **55**, 249 (1922).

[55] DeRight, R. E., and Wiig, E. O., *J. Am. Chem. Soc.*, **57**, 2411 (1935).

[56] Emschwiller, G., *Compt. rend.*, **198**, 1151 (1934).

[57] Emschwiller, G., *Compt. rend.*, **198**, 464 (1934).

An iodine-sensitized decomposition of ethylene iodide in carbon tetrachloride is discussed by Dickinson and Nies.[58] Emschwiller[59] writes for the decomposition of diiodoethane,

$$CH_3CHI_2 + h\nu \longrightarrow CH_2 = CHI + HI$$

$$CH_3CHI_2 + HI \longrightarrow CH_3CH_2I + I_2$$

Both products then decompose with the separation of iodine, so that the complete reaction may be written:

$$4CH_3CHI_2 \longrightarrow C_2H_2 + 2C_2H_4 + C_2H_6 + 4I_2.$$

The ethylene then mostly forms ethylene iodide. In the presence of oxygen, both diiodoethane and unsymmetrical diiodoethylene are completely oxidized. The analogy of structure between diiodomethane and diiodoethane implied by a similarity of decomposition is confirmed by the similarity of their absorption spectra and by the rapid photochemical oxidation of diiodomethane.

Iodoform, although said to be very light-stable in the absence of oxygen, may in benzene solution yield some iodine and hydriodic acid in daylight.[60] Chloroform is also stable, although it exhibits a continuous absorption beginning at 2530A (1 cm. of liquid) or at 2300A (50 cm. of vapor at 1 mm.). Hill[61] was unable to detect any decomposition in a static system. In streaming vapor, chlorine could not be detected, but hydrogen chloride was formed. There was evidence of a short-chain reaction, yielding four molecules per quantum absorbed. The yield was not affected by the presence of hydrogen. It seemed to be increased by nitrogen and was very greatly increased by oxygen, but in the latter case the mechanism is doubtless changed. Binz and Hughes[62] have suggested that sodium triiodomethanesulfonate, proposed for x-ray work in urological diagnosis, may owe its observed toxicity to the ease with which it splits off iodine in light.

Carbon tetrachloride has been suggested as an actinometric compound for standardizing the ultraviolet output of mercury arcs,[63] at wave-lengths less than about 2650-2750A, but Hymas[64] could not obtain satisfactory results with it. According to Benrath and Hertel,[65] decomposition may be represented as

$$2CCl_4 \longrightarrow C_2Cl_6 + Cl_2$$

the reaction occurring in the liquid exposed in an open vessel. In a recent investigation, Lyons and Dickinson[66] found that in the absence of oxygen, pure carbon tetrachloride underwent practically no decomposition when exposed to the 2537A line, the quantum yields being less than 0.01. In the presence of oxygen, however, phosgene and chlorine were produced in equimolar proportions, the quantum yield being close to unity.

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[58] Dickinson, R. G., and Nies, N. P., *J. Am. Chem. Soc.*, **57**, 2382 (1935).

[59] Emschwiller, G., *Compt. rend.*, **199**, 854 (1934).

[60] Dubrisay, R., and Emschwiller, G., *Compt. rend.*, **195**, 660 (1932)

[61] Hill, D. G., *J. Am. Chem. Soc.*, **54**, 32 (1932); see also Massol, G., and Faucon, A., *Compt. rend.*, **159**, 314 (1914); *Bull. soc. chim.*, **19**, 350 (1916).

[62] Binz, A., and Hughes, B., *Ber.*, **68B**, 1513 (1935).

[63] MacKenzie, T. C., and King, A. A., "Practical Ultraviolet Light Therapy," New York, Wood 1926.

[64] Hymas, F. C., *Quart. J. Pharm.* **2**, 281 (1929).

[65] Benrath, A., and Hertel, E., *Z. wiss. Phot.*, **23**, 30 (1924)

[66] Lyons, E. H., Jr., and Dickinson, R. G., *J. Am. Chem. Soc.*, **57**, 443 (1935).

Trichloroethylene may be oxidized in the presence of chlorine as sensitizer by the 4360A line.[67] The yield of dichloroacetyl chloride is not greater than 95 per cent. The rate varies with the light intensity, but is independent of the trichloroethylene and oxygen concentrations. The quantum yield is about 40 at 95°. A peroxide, $C_2HCl_4O_2$, may be a part of the chain.

In the case of tetrachloroethane,[68] the reaction probably consists in a primary decomposition into HCl and $CHCl_2CCl$, the latter then reacting with oxygen to form dichloracetyl chloride, which is hydrolyzed by moisture to dichloracetic acid. Oxygen also removes a hydrogen atom from the original halide, and the $CHCl_2CCl_2$ residues combine to form octachlorobutane. In dry air, a fuming liquid, dichloracetyl chloride, could be obtained. The reactions were shown not to be due to ozone produced by the action of the light upon the oxygen. In the presence of nitrogen rather than air, no reaction whatever occurred, not even the evolution of hydrogen chloride.[69] The same was true of the compounds $CHCl_2CCl_3$ and $CCl_2{=}CHCl$. The reaction was therefore assumed to be brought about by activated oxygen. Further evidence for this mechanism is found in the fact that the compound $(CH_2Cl)_2$ can react, although it does not absorb in the wave-length range employed. In the presence of dry oxygen in short wave-length light, it gives monochloracetic acid.[70]

Attention has been called to a bromine-sensitized photochemical decomposition of dibromotetrachloroethane by Carrico and Dickinson.[71] It proceeds as a chain reaction with quantum yields which, at low intensities, are independent of the intensity, but which fall off at higher intensities.

There is a bromine-sensitized oxidation of carbon tetrabromide in carbon tetrachloride, produced by the 4360A line, which may be expressed by

$$2CBr_4 + O_2 \rightarrow 2COBr_2 + 2Br_2 \quad [72]$$

Not more than 50 kcal. is required to remove the first bromine atom.

ALCOHOLS

Bielecki and Henri[73] found the absorption of ethyl alcohol to begin at about 2500A.

Several new methods for the purification of alcohol for use as a solvent in absorption spectroscopy were tested by Leighton, Crary and Schipp[74] They found the threshold absorption furthest in the ultraviolet for samples which had been allowed to stand for one week over active aluminum amalgam, filtered and distilled Their results were in general confirmed by Harris,[75] who preferred, however, to modify the method of preparation introduced by Castille and Henri[76] by carrying out the final distillation with the aid of zinc wool rather than zinc powder.

Herzberg and Scheibe[77] found that both methanol and ethanol vapors show continuous absorption beginning at about 2000A and extending to 1500A. They believed a decomposition into alkyl and hydroxyl radicals to be probable. Terenin and Neuïmin[78] find that methanol when decomposed in the Schumann region emits bands indicative of the presence of hydroxyl radicals in excited states. From studies of the continuous absorption of a number of alcohols in the vapor state, Fukumoto[79] reports the energy of dissociation of the carbon to hydroxyl bond to vary from 133.6 to 152.2 kcal. per mole for the series from methanol to n-$C_{12}H_{25}OH$. For the isomers of butyl alcohol, no regularity was to be found in the energy of this bond, although it was at a maximum, 141.9 kcal., in the normal alcohol.

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[67] Muller, K. L., and Schumacher, H J, *Z. physik. Chem.*, **37B**, 365 (1937).

[68] Müller, E., and Luber, A., *Ber*, **65B**, 985 (1932).

[69] Müller, E., and Ehrmann, K, *Ber.*, **69B**, 2207 (1936)

[70] Aromatic compounds with halogen in the side chain behave similarly, benzyl chloride slowly changing into benzoic acid and $C_6H_5CHCl_2$ yielding benzoyl chloride.

[71] Carrico, J. L., and Dickinson, R G, *J Am Chem Soc.*, **57**, 1343 (1935).

[72] Koblitz, W., Meissner, H., and Schumacher, H J., *Ber*, **70B**, 1080 (1937).

[73] Bielecki, J., and Henri, V, *Ber*, **45**, 2819 (1912), *Compt. rend*, **155**, 456 (1912).

[74] Leighton, P. A, Crary, R. W., and Schipp, L T., *J. Am. Chem. Soc.*, **53**, 3017 (1931).

[75] Harris, L., *J Am. Chem. Soc.*, **55**, 1940 (1933).

[76] Castille, A., and Henri, V., *Bull soc. chim biol.*, **6**, 299 (1924); *Chem. Abs.*, **18**, 3165 (1924).

[77] Herzberg, G., and Scheibe, G., *Z. physik. Chem.*, **7B**, 390 (1930).

The alcohols are stable to ultraviolet rays,[80] unless the wave-lengths be shorter than about 2000A. Methanol and ethanol are decomposed by such wave-lengths.[81] Methanol gives some formaldehyde, but most is decomposed into hydrogen and carbon monoxide. Indeed, the products of the alcohol[82] decomposition are said to be about 80 per cent hydrogen and 20 per cent carbon monoxide. (Ethanol gives hydrogen and acetaldehyde.) There is as yet no evidence for the formation of atomic hydrogen. The quantum yield is between one and two.[83] From the failure of the para-ortho hydrogen test for free radicals, Patat did not believe the primary process could be the dissociation of the carbon-hydroxyl bond suggested by spectroscopic observations.

Elhart and Orth[84] state that goldfish are anesthetized more rapidly in methanol or ethanol solutions when these are irradiated because of the formation of aldehyde and acid.

Cantieni[85] finds that in the presence of oxygen, methanol forms peroxide in the absence of water, the presence of which retards its formation. The peroxide CH_3OOH is assumed to oxidize methanol in the presence of ultraviolet light with the production of traces of formaldehyde. Peroxide formation occurs most rapidly with isoalcohols, rapidly with methanol and more slowly in the remaining normal alcohols. In ultraviolet light of longer wave-lengths the rate of formation of peroxides increases with an increase in the number of carbon atoms in the alcohol. Cantieni also finds glycol to form a peroxide $HO{\cdot}CH_2CH_2O_2H$. This, reacting with excited glycol molecules, gives carbon dioxide, water and glycol.[86]

According to Henri and Ranc,[87] glycerol, as such or better in aqueous solutions, suffered some decomposition, especially in the presence of air. A small quantity of a substance giving a positive phloroglucinol reaction for glyceric aldehyde was formed. In alkaline solution, β-acrose was apparently identified by means of the phenylosazone. Its amount could possibly be increased by the addition of salts of iron, cobalt or uranium before the irradiation. Formaldehyde and acids were also formed.[88] Cantieni[89] finds glycerol irradiated in solutions of various concentrations, to give carbon dioxide and water, a peroxide, $OH{\cdot}CH_2CH(OH)CH_2OOH$ being postulated as an intermediate product. The evidence for the formation of the intermediate in this and other alcohol oxidations consisted in a titanium sulfate titration.

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[78] Terenin, A., and Neuïmin, H., *Nature*, **134**, 255 (1934); *J. Chem. Physics*, **3**, 436 (1935).

[79] Fukumoto, Y., *Nature*, **134**, 538 (1934).

[80] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **156**, 68 (1913); Volmar, *Compt. rend.*, **182**, 1607 (1926).

[81] Patat, F., *Anz. Akad. Wiss. Wien. Math-naturw. Kl.*, 93 (1933); *Chem. Abs.*, **28**, 6371 (1934); Patat, F., and Hoch, H., *Z. Elektrochem.*, **41**, 494 (1935).

[82] Fricke, H., and Hart, E. J., *J. Chem. Physics*, **4**, 418 (1936) believe methanol to give directly hydrogen and formaldehyde.

[83] 0.8 for ethanol in solution, according to Farkas, L., and Hirschberg, Y., *J. Am. Chem. Soc.*, **59**, 2450 (1937). Isopropyl alcohol yields acetone and hydrogen. One of the hydrogen atoms comes from the OH and the other from C—H.

[84] Elhart, W., and Orth, O. S., *Anesthesia and Analgesia*, **14**, 15 (1935); *Chem. Abs.*, **29**, 3401 (1935)

[85] Cantieni, R., *Ber.*, **69B**, 1101, 1386 (1936). *Cf.* Milas, N., U. S. P. 2,115,206-7, April 26, 1938, *Chem. Abs.*, **32**, 4606 (1938).

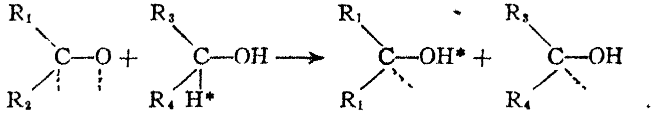
[86] Cantieni, R., *Z. wiss. Phot.*, **36**, 116 (1937).

[87] Henri, V., and Ranc, A., *Compt. rend.*, **154**, 1261 (1912); Bierry, H., Henri, V., and Ranc, A., *Ibid.*, **152**, 535 (1911).

The oxidation of ethyl alcohol can be photosensitized by the addition of hydrogen peroxide. The oxidation is a chain reaction of short chain length, compatible with that of the chains postulated in the Haber-Willstätter mechanism of the chain reactions set up in the enzymatic oxidation of alcohol.[90]

The hydrogen peroxide-sensitized oxidation of mannitol known to Henri and Ranc, (l.c.) has recently been studied by Salley.[91] At a constant initial hydrogen peroxide concentration, increase in the mannitol concentration causes an increase in the rate of absorption of oxygen and a simultaneous decrease in the rate of decomposition of the hydrogen peroxide. At a sufficiently high mannitol concentration, however, the rates of both reactions become independent of the mannitol concentration. Since a maximum of two molecules of oxygen can be absorbed for each molecule of hydrogen peroxide which disappears, the photosensitized oxidation of the mannitol does not appear to be a chain process. In the presence of ethylamine, an inhibitor of the photolysis of hydrogen peroxide, the rate of the decomposition of the peroxide in the mannitol mixture is increased. At the same time, the rate of absorption of oxygen apparently decreases, probably owing to the destruction of the hydrogen peroxide with some evolution of oxygen.

Ketones and alcohols undergo mutual oxidation in light, according to Weizmann, Bergmann and Hirschberg,[92] who cite the earlier observations. Acetophenone and butanol give the pinacol of acetophenone, butanol being dehydrogenated to butyraldehyde. Acetophenone reacts in an analogous fashion with cyclohexanol, phenylmethylcarbinol, ethanol and isopropanol. The system cyclohexanone-cyclohexanol gives but a poor yield of cyclohexanone pinacol. The system acetone-butanol gave two isomeric forms of *sym*-dipropylglycol, and, in the first fractions of the reaction product, butyraldehyde and isopropanol. It is assumed that the first step in these processes is the activation of the carbonyl compound leading to a diradical form which reacts with the carbinol, splitting the C—H bond and giving two radicals. These subsequently stabilize by symmetrical or unsymmetrical dimerization or by a second oxidation-reduction process.



A photocatalytic influence of ketones on the velocity of oxidation of ethyl and other alcohols was described by Cohen.[93] The velocity was found to be independent of the concentration of the ketone within wide limits and proportional to the alcohol concentration.[94] The ketone itself either remains unchanged or forms a pinacone. Either benzophenone, aliphatic α-diketones or α, β-diketones with an aromatic nucleus could be employed. No absorption peak in the ketone spectrum appeared to coincide with the wave-length range which proved active (4000-4100A).

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[88] Henri, V., and Ranc, A., *Compt. rend.*, **151**, 316 (1910); *Biochem Z.*, **64**, 257 (1914).

[89] Cantieni, R., *Ber.*, **69B**, 1796 (1936).

[90] Taylor, H. S., and Gould, A. J., *J. Am. Chem. Soc.*, **55**, 859 (1933); *J Phys. Chem.*, **37**, 367 (1933).

[91] Salley, D. J., *J. Phys. Chem.*, **38**, 465 (1934).

[92] Weizmann, C., Bergmann, E., and Hirschberg, Y., *J. Am. Chem. Soc.*, **60**, 1530 (1938).

[93] Cohen, W. D., *Proc. Acad. Sci. Amsterdam*, **26**, 443 (1923); *Chem. Abs.*, **14**, 2785 (1920); **15**, 3617 (1921); **18**, 50 (1924); Boeseken, J., *Rec. trav. Chim.*, **40**, 433 (1921); **39**, 243 (1920). See also Chapter 25.

Boeseken and Langedijk employed the reaction to effect a partial asymmetric synthesis. The *l*-menthyl ester of *o*-$PhCOC_6H_4COOH$ was used to catalyze the oxidation of racemic methylethylcarbinol and caused after a hundred hours a levorotation of between 0.03 and 0.04° in a 20-cm. tube.

Berthoud[95] concluded that, at least in the case of benzophenone, it is the ultraviolet absorbed by the ketone which is active. He also found the rate proportional to the intensity of the ultraviolet rather than, as the earlier workers believed, to the square of the visible light intensity. For complete absorption of the available light, the rate, after an induction period of 30 to 60 minutes, reached a steady value inversely proportional to the concentration of oxygen. At 3660A, the quantum yield for oxygen consumed was 18 and the temperature coefficient was 1.7.

Benzoquinone also effects the oxidation of alcohols when irradiated by the wave-lengths 4050, 4080 or 4360A; the quantum yields are unity.[96]

The action of sunlight on the oxidation of alcohols by powdered potassium dichromate[97] produces only aldehydes. With methyl alcohol, the dichromate is reduced to chromic hydroxide and with ethyl alcohol to a brown powder of unknown composition. The ratio of the yield of aldehyde to the quantity of dichromate reduced increases with the time of exposure and reaches after 12 to 24 hours a value of two. With large quantities of dichromate present, the yield of aldehyde drops because of the screening effect of the precipitates formed and of the dichromate itself. Plotnikow,[98] as well as Bowen and co workers,[99] used the dichromate ion in solution. Plotnikow described a wide variety of photoöxidations effected by this compound. Ethylene glycol rapidly becomes alkaline and deep green, glycolaldehyde and glyoxal being produced. Glycerol solutions yield glyceric aldehyde and acid and dihydroxyacetone. Propyl alcohol gives propionaldehyde and traces of propionic acid, and isopropyl alcohol acetone and acetic and formic acids. Amyl alcohol yields an aldehyde and a brown precipitate of a chromium chromate.

Bowen emphasized the fact that, although in acid solutions the aldehyde is formed without the production of any chromium precipitate, in neutral solutions there results a precipitate of uncertain composition. In neutral and alkaline solutions, the chromate ion present is photochemically inactive. The quantum efficiency is independent of the light intensity, of added acid (if not too little is present), of temperature and of the dichromate ion concentration between 0.1 and 0.01*N*. Only the ion $HCrO_4^-$ is effective. In strongly alcoholic solutions the quantum yield is approximately one, but in weaker solutions it is diminished.

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[94] Boeseken, J., and Langedijk, S L., *Proc Acad Sci Amsterdam*, **35**, 1124 (1926); Boeseken, J., Cohen, W. D., and Langedijk, S L., *Rec trav. Chim.*, **46**, 383 (1927).

[95] Berthoud, A., *Helv. Chim Acta*, **16**, 592 (1933).

[96] Berthoud, A., and Porret, D., *Helv. Chim. Acta*, **17**, 694 (1934), see also work of Leighton and Forbes discussed under actinometers in Chapter 7.

[97] Schwarz, M., *Z. Elektrochem.*, **32**, 15 (1926)

[98] Plotnikow, J., *Chem. Ztg.*, **52**, 669 (1928); Cantieni, R., *Ber.*, **69B**, 2282 (1936) believes the reaction proceeds through a peroxide.

[99] Bowen, E. J., and Bunn, C. W., *J. Chem. Soc.*, 2353 (1927); Bowen, E. J., and Yarnold, E T., *Ibid.*, 1648 (1929); Bowen, E. J., Peacocke, T. A., and Wellburn, E. R., *Ibid.*, 1866 (1931); Bowen, E. J., and Chatwin, J. E., *Ibid.*, 2081 (1932).

Vith increasing hydrogen ion concentration, the yield increases to a limit of 1.8 or wave-lengths between 4360 and 3665A.[100]

Potassium ferrocyanide solution gives an orange coloration with isobutyl lcohol, especially in light.[101]

ETHERS

It has been noted[102] that some samples of commercial ether develop peroxides vhen exposed to ultraviolet rays and so are unsuitable for use in the tropics, lthough they satisfy all the usual tests for purity. Irradiation may be employed n testing the stability of various samples. Although Athias[103] believes atmosheric oxygen to be concerned in the decomposition of ether in light, Binz[104] ound the photochemical formation of peroxides to be independent of the presence f atmospheric oxygen. Little is known of the nature of the reaction.

In the presence of uranyl nitrate, sunlight is capable of forming oxalic acid rom ether, according to Rowell and Russell.[105] They suggest that the light educes the uranyl to the uranous ion and oxidizes the ether to diglycol, of which art is oxidized to diglycollic acid and part hydrolyzed to glycol, which is further xidized to oxalic acid.

Milas[106] found the rate of peroxide formation in ethers to depend largely on he type of groups attached to the oxygen atom. Ultraviolet light greatly accelrated the rate of autoxidation of dibenzyl ether in particular.

Acetone photosensitizes dimethyl ether vapor, the rate of decomposition varyng with the concentration of the ether, the square root of the absorbed light and nversely as the square root of the acetone concentration.[107] The quantum yields ased on carbon monoxide formed were as low as 5 and as high as 230 depending pon the light intensity and total pressure. With diethyl ether, the quantum ields were one-tenth as great under similar conditions.

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[100] See also Fugassi, P., *J. Am. Chem. Soc.*, **59**, 2092 (1937).

[101] Kutzlnigg, A., *Z. anal. Chem.*, **77**, 349 (1929); for the action of quinones on alcohols, see Chaper 25.

[102] Liversedge, S G., *Analyst*, **59**, 815 (1934); *Brit Chem Abs*, **B**, 173 (1935).

[103] Athias, F., *Thesis (Algiers)*, **1924**; *Chim. et ind*, **14**, 744 (1925); *Chem. Abs.*, **20**, 478 (1926); atsunami, S., *J Pharm. Soc. Japan*, *No.* **520**, 529 (1925); *Chem. Abs.*, **20**, 478 (1926).

[104] Binz, C., *Suddeut. Apoth. Ztg.*, **70**, 128 (1930).

[105] Rowell, S. W., and Russell, A S, *J. Chem. Soc.*, **127**, 2900 (1925)

[106] Milas, N. A., *J. Am. Chem. Soc.*, **53**, 227 (1931).

[107] Leermakers, J. A., *J. Am Chem. Soc.*, **56**, 1899 (1934).

Chapter 23

The Behavior of Unsaturated Compounds

The compounds discussed in the preceding chapter have been relatively inert photochemically, reacting (if at all) with low quantum yields, except in the case of sensitized processes or in reactions in which the light is absorbed by some other reactant. It has long been known that in ring compounds the presence of double bonds is usually necessary for marked absorption of the longer ultraviolet wave-lengths. Of the olefinic compounds, ethylene exhibits absorption which begins at 2100A and is nearly complete at 1850-1990A, a region in which ethane exhibits no absorption. The introduction of various substituents in molecules containing a double bond frequently displaces the absorption to longer wave-lengths. Particularly effective is the presence of one or more conjugated double bonds, as Smakula has recently demonstrated.[1]

Several possible types of reactions may follow upon the absorption of light by double bonds. Usually only one of the two carbon-to-carbon linkings is broken. Polymerization may result, two or more of the photochemically produced molecules with free valences combining. In an absorbing compound with substituents on each carbon atom adjacent to the double bond, after absorption of energy has broken one linkage, there may be a rotation about the remaining linking so that when molecules suffer a collision the double bond may be reformed with the production of the stereoisomer of the original compound. More rarely, and particularly when the shorter wave-lengths have been absorbed, the energy is transferred within the molecule to alkyl groups, which may be decomposed with evolution of hydrogen and formation of compounds with triple linkages.

SIMPLE DECOMPOSITIONS

Mooney and Ludlam[2] have shown that ethylene can be decomposed by wave-lengths shorter than 2100A, giving acetylene and hydrogen, together with a small amount of a polymerized product.[3] The long wave-length limit of 2110A corresponds with the heat of dissociation of ethylene into acetylene and hydrogen, 135 kcal. According to McDonald and Norrish,[4] ethylene at low pressures when irradiated in the fluorite region deposits a polymer and forms hydrogen and a condensible gas composed of at least two fractions.

In the presence of excited mercury atoms, ethylene is first slightly decomposed and then the remainder is polymerized.[5] In the presence of hydrogen, ethane is formed, the rate being proportional to the square root of the hydrogen concentration. Taylor and Hill[6] agree that saturated hydrocarbons are formed, but note that they are subsequently decomposed both by the excited mercury atoms and by atomic hydrogen. Methane is the stable product formed in the gas phase and a liquid polymer C_xH_{2x} is deposited on the walls. Jungers and Taylor[7] find the mercury-sensitized hydrogenation more rapid in the case of deutero-ethylene than of ethylene. Methane is formed only in negligible amounts, butane being the important product with small amounts of ethane. At low hydrogen concentrations, a photosensitized polymerization occurs; it is slower in the deuterium compound.

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[1] Smakula, A., *Angew. Chemie*, **47**, 657 (1934).

[2] Mooney, R. B., and Ludlam, E. B., *Trans. Faraday Soc.*, **25**, 442 (1929).

[3] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **155**, 207 (1912); Klever, H. W., and Glaser, F., *Mitt. Chem.-tech. Inst. Tech. Hochschule Karlsruhe*, No. **1**, 1 (1922); *Chem. Abs.*, **18**, 1976 (1924).

[4] McDonald, R. D., and Norrish, R. G. W., *Proc. Roy Soc.*, **157A**, 480 (1936).

[5] Olson, A. R., and Meyers, C. H., *J. Am. Chem. Soc.*, **48**, 389 (1926).

[6] Taylor, H. S., and Hill, D. G., *J. Am. Chem. Soc.*, **51**, 2922 (1929).

In the presence of oxygen, irradiation of ethylene produces some formic acid.[8] In general, in ethylenic and acetylenic compounds in the presence of oxygen, the double and triple linkages are ruptured and simple acids are formed. In the presence of ammonia, cyclic compounds are produced. Ethylene, for example, first yields amino-ethylenes; then ring formation takes place with production of compounds of the pyrrolidine and pyridine types, which may be regarded as the mother substances of alkaloids. According to Milas, Kurz and Anslow,[9] hydrogen peroxide reacts with double-bonded compounds on exposure to ultraviolet light to form glycols, possibly because of a decomposition to two hydroxyl radicals. By this reaction, glycerol, dihydroxybutyric acid, *meso*-tartaric acid and its diethyl ester have been prepared from allyl alcohol, crotonic acid, maleic acid and its diethylester, respectively.

Trichloroethylene undergoes a chlorine-sensitized photo-oxidation at 4360A to dichloroacetyl chloride. It is a chain reaction (quantum yield 40) of zero order with respect to the trichloroethylene and oxygen. The rate is proportional to the absolute intensity of the light absorbed.[10]

Matthews and Elder[11] produce compounds of sulfur dioxide and unsaturated hydrocarbons by direct combination by exposing the mixed liquids to sunlight or ultraviolet rays, or in some cases by heating. The examples given are the compounds with pseudo-butylene $(C_4H_8SO_2)_n$, propylene, amylene and ethylene. The butylene product is a horny or glassy, clear white solid, soluble in chloroform or tetrachloroethane and not easily flammable. It can be used for making varnishes, transparent films, etc., and may be mixed with celluloid by first softening both with acetone. It renders the celluloid less flammable. Work on this reaction has been reviewed by Snow and Frey,[12] who find from their own experiments that the reaction occurs in the liquid phase, the effective wave-length range being 3000 to 3800A. It is catalyzed by oxygen, organic peroxides, hydrogen peroxide, but is inhibited by nitric acid or hydrogen sulfide and is slowed at high temperatures.

Uranium salts sensitize various ethylenic compounds as well as aldehydes to sunlight. Acetylenic compounds react even more readily,[13] aldehyde and formic acid being produced. Amylene yields amyl alcohol. Cyclohexenes, but not cyclohexanes, behave similarly, but benzene does not react in the absence of a side-chain.

The photochemical reduction of sodium dichromate by ethylene glycol has been found to be affected by the presence of water.[14] For equal amounts of light, the ratio of the reductions occurring in one hour with water present and with it absent was 59 to 79. Within the range of 0.2 to 0.6 per cent concentrations of the dichromate in the glycol, the amount of decomposition was proportional to the time.

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[7] Jungers, J. C., and Taylor, H. S., *J. Chem. Phys.*, **6**, 325 (1938).

[8] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1327 (1910).

[9] Milas, N., Kurz, P. F., and Anslow, W. P., *J. Am. Chem. Soc.*, **59**, 543 (1937).

[10] Müller, K. L., and Schumacher, H. J., *Z. physik Chem.*, **B37**, 365 (1937).

[11] Matthews, F. E., and Elder, H. M., British P. 11,635, May 11, 1914; Reports Progress Applied Chem., **1**, 192 (1916).

[12] Snow, R. D., and Frey, F. E., *Ind. Eng. Chem.*, **30**, 176 (1938).

[13] Aloy, J., and Valdiguié, A., *Bull. soc. chim.*, **37**, 1135 (1925).

Reactions in which halogens are added at the double bond are considered in Chapter 28.

POLYMERIZATION

Berthelot and Gaudechon[15] observed that ultraviolet rays polymerize ethylene to a liquid having the odor of rancid fat, and boiling below 100°C. According to Taylor and Emeléus,[16] the polymerization of ethylene can be sensitized to the light of the mercury arc by means of ammonia, the rate of the reaction increasing with the ammonia concentration. The formation of saturated hydrocarbons in the reaction system with varied ratios of hydrogen to ethylene is subordinate to the polymerization process. An oil is produced which probably contains the nitrogen of the ammonia decomposed in the process. Emeléus and Taylor[17] found methylamine and ethylamine to induce a similar photopolymerization of ethylene at temperatures above 200°C. Jungers and Taylor[18] find that ethylene cannot be polymerized in quenching the resonance radiation of sodium, possibly because of unfavorable localization of the energy received by the ethylene in the quenching process. It can be induced, however, by the photodecomposition of admixed acetone, due to an effect of radicals from the latter. It is also polymerized by ethyl radicals produced by the mercury-sensitized photodecomposition of ethyl iodide.[19]

Commercial gaseous butadiene, containing 30 per cent pseudobutylene, but not the pure bivinyl gas, is polymerized in the light of the quartz lamp to a white solid, insoluble in alcohol, ether or benzene[20] Khokhlovkin[21] found a sample of butadiene completely autopolymerized in light (shorter than 2300A) and air at room temperature in 515 days. At 45°C., it occurred in 100 hours. Light considerably increased the rate of the autocatalytic process. Gee[22] finds the quantum yield (0.3) of a mercury-sensitized polymerization nearly independent of the pressure. The main product was an insoluble polymer, with some hydrogen and a cyclic dimer, the latter occurring in greatest proportion at low pressures. 2-Butoxy-1,3-butadiene in ultraviolet light for one week gives 13 per cent of a polymer which is somewhat sticky and elastic.[23]

Ferrer[24] reports that diphenylene ethylene, $(C_6H_4)_2C{:}CH_2$, is stable for several hours in the dark, but is completely polymerized and rendered insoluble in ether, when exposed for ten minutes to the mercury arc.

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[14] Riesenfeld, E. H., and Hecht, O., *Z. wiss. Phot.*, **26**, 369 (1929); *Brit. Chem Abs.*, **1929A**, 895.

[15] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1169 (1910).

[16] Taylor, H. S., and Emeléus, H. J., *J. Am. Chem. Soc*, **52**, 2150 (1930); **53**, 573 (1931).

[17] Emeléus, H. J., and Taylor, H. S., *J. Am. Chem. Soc.*, **53**, 3370 (1931).

[18] Jungers, J. C., and Taylor, H. S., *J. Chem. Physics*, **4**, 94 (1936), *Chem. Abs*, **30**, 2109 (1936); *Trans. Faraday Soc.*, **33**, 1353 (1937); *Brit. Chem. Abs.* **A**, 574 (1937).

[19] Joris, G. G., and Jungers, J. C., *Bull. soc. chim. Belg.*, **32**, 4426 (1938); *Chem. Abs.*, **32**, 4426 (1938).

[20] Nikiforov, V. K., and Runtzo, P. M., *Acta Physicochim. U.R.S.S.*, **3**, 335 (1935); *Chem. Abs*, **30**, 2493 (1936).

[21] Khokhlovkin, M. A., *Sintet Kauchuk, No.* 4. 12 (1936), *Chem. Abs.*, **30**, 6602 (1936); see also Kublitskii, A. M., *Sintet Kauchuk (U.S.S.R.)*, No. 7-8, 30, 1936; *Chem. Abs.*, **31**, 6503 (1937).

[22] Gee, G., *Trans. Faraday Soc.*, **34**, 712 (1938)

[23] Dykstra, H. B., *J. Am. Chem. Soc.*, **57**, 2255 (1935).

[24] Ferrer, J., *Anales soc. espan. fis. quim.*, **20**, 459 (1922); *Chem. Abs.*, **17**, 3177 (1923).

Vinyl chloride and vinyl bromide polymerize rapidly when exposed to light. The chloride forms an amorphous insoluble substance of specific gravity 1.406, which melts above 130°C., with decomposition.[25] The polymerized bromide is likewise insoluble in water, alcohol, or ether, has a specific gravity of 2.075 and begins to decompose at 125 to 130°C. Plotnikow[26] stated the properties of the vinyl chloride polymer, probably $(CH_2CHCl)_{16}$, formed by the extreme ultraviolet rays of a mercury arc, to be those of a "synthetic rubber." Sunlight is effective only in the presence of catalysts, such as the salts of manganese, cobalt, nickel, copper and vanadium and most especially, the uranyl salts. A 2.5-per cent solution of vinyl chloride in methyl alcohol was employed in the apparatus shown in Figure 115. Carbon tetrachloride accelerated the transformation. The white precipitate obtained dissolves in many organic solvents to form colloidal systems varying from paste to solid.

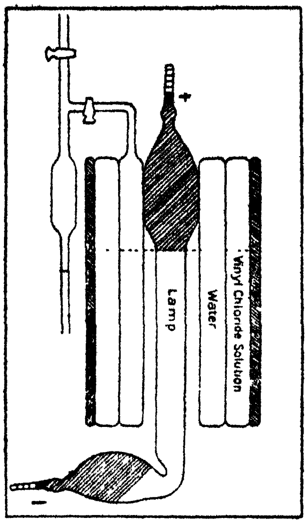

FIGURE 115.

Apparatus for Synthesizing "Rubber" from Vinyl Chloride. A water-cooled jacket prevents overheating of the vinyl chloride solution.

Courtesy "India Rubber World"

Ostromuislenski[27] obtained by the polymerization of vinyl bromide a material which he termed caouprene bromide. This exists in three forms, called α, β and γ. When the α and β forms are submitted to the action of ultraviolet the γ form is yielded.

It is claimed[28] that if the polymerization of vinyl chloride by sunlight or ultraviolet rays, with or without a catalyst such as a soluble lead salt, is continued beyond the acetone-soluble or α-stage, a new β-modification, insoluble in acetone but soluble in monochlorobenzene, is obtained before conversion into the γ- or δ-forms. The new form may also be obtained from the γ and δ forms by heating them with aniline, quinoline, etc. Monochlorobenzene solutions of the new product to which is added a plasticizer, *e.g.*, a dichlorobenzene, yield flexible, transparent and non-flammable films on drying. The β-product is also obtainable from the α-compound by prolonged action of ultraviolet rays and heat or by heat alone.[29]

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[25] Baumann, E., *Annalen*, **163**, 317 (1872).
[26] Plotnikow, J., *Z. wiss. Phot.*, **21**, 117 (1922); *Chem. Abs.*, **16**, 1337 (1922).
[27] Ostromuislenski, I., *J. Russ. Phys. Chem. Soc.*, **44**, 204 (1912).
[28] Van Dyk, L. A., British P. 255,837, June 29, 1926; *Brit. Chem. Abs.*, **1927B**, 564.

A vinyl halide may also be condensed with a phenol in the presence of aluminum or ferric chloride, before polymerization by ultraviolet light.[30]

According to Guyer and Schütze,[31] 0.1 per cent of hydroquinone prevents the polymerization of vinyl bromide in direct sunlight for several months.

Stobbe and Toepfer[32] report that *p*-vinylanisole is polymerized when placed in glass tubes in direct sunlight, the extent of reaction being about the same after four days' exposure as after four hours at 100°C. in the dark. If a little of the polymeric form is added, the polymerization proceeds as far in one day as it does in four with the pure substance. When *p*-vinylanisole in quartz tubes at 30°C. is alternately irradiated by a quartz mercury lamp and kept dark, polymerization appears not to proceed during the period of raying, but during the following periods of darkness. It is believed that polymerization by rays of wave-lengths longer than 3300A may be reversed by rays of shorter wave-length.

The polymerization of vinyl esters gives rise to various useful products.[33] It may be accelerated by benzoyl peroxide, ozonides, and by anhydrides of organic acids used in conjunction with agents yielding oxygen, as perborates, percarbonates, silver oxide, etc. The polymerization products are solid, colorless and transparent celluloid-like masses which are odorless and can be turned, cut, planed and otherwise manipulated to form various articles. These solids, rendered plastic in hot water, can be molded; upon cooling, the material hardens again. Chlorinated esters may also be polymerized by heat and light in a two-stage operation and employed in lacquers.

Oxygen inhibits the photopolymerization of vinyl acetate, the temperature coefficient of which is markedly greater than unity. The quantum yield is 1.7 at 2300A, 1.2 at 2536A and 936 with a 3000 to 4000A band, indicating a chain mechanism.[34] The effects of various inhibitors in ethyl acetate as solvent have been studied by Jeu and Alyea,[35] who followed the rate of the reaction by measuring the unsaturation by means of Wijs' solution. Among sixteen representative inhibitors, which include alcohols, esters, acids, amines, oximes, phenols, aldehydes and alkaloids, the relative inhibitory power is approximately the same for this reaction as for the oxidation of sodium sulfite. There is, however, no obvious relation to their effects on the photolysis of hydrogen peroxide. Pyrogallol is about 3200 times as effective an inhibitor as is ethyl alcohol.

Groff[36] described a highly plastic composition formed by fluxing on hot differential rolls (100-120°C.) and sheeting out, a mixture of 100 parts vinyl resin (formed by polymerization of 80 parts vinyl chloride and 20 parts vinyl acetate), 60 parts ethylene glycol monoethyl ether diester of ethylene glycol phthalate, 1 part carnauba wax, 1 part calcium stearate and 1 part calcium hydroxide. Exposure for 100 hours to radiation from a mercury arc at a distance of 20 inches caused only a slight discoloration and did not affect the flexibility.

Vinylethinylcarbinols may be polymerized by the action of air, light or both;

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[29] Van Dyk, L. A., British P. 260,550, July 26, 1926, *Brit Chem. Abs*, **1927B**, 564.

[30] British Celanese, Ltd., British P. 409,132, April 18, 1933; *Brit. Chem. Abs.* **B**, 534 (1934).

[31] Guyer, A., and Schütze, H., *Helv. Chim. Acta,* **17**, 1544 (1934).

[32] Stobbe, H., and Toepfer, K., *Ber.*, **57B**, 484 (1924); *Chem. Abs.*, **18**, 2503 (1924).

[33] Klatte, F., and Rollett, A., U. S. P. 1,241,738, Oct. 2, 1917; *cf.* Kuhl, H., *Reports of the Progress of Applied Chemistry, Soc. Chem. Ind.*, **1**, 192 (1916); *J. Soc. Chem. Ind.*, **34**, 623 (1915).

[34] Vernon, A. A., and Taylor, H. S., *J. Am. Chem. Soc*, **53**, 2537 (1931).

[35] Jeu, K-K., and Alyea, H. N., *J. Am. Chem. Soc.*, **55**, 575 (1933).

[36] Groff, F., U. S. P. 1,966,856, July 17, 1934, to Carbide and Carbon Chemicals Corp.

the process is accelerated by the use of halides such as those of zinc, iron, aluminum, antimony, bismuth, boron and tin, organic peroxides such as benzoyl peroxides or acetyl peroxide, ozone, hydrogen peroxide or persalts, or by accelerators of the photochemical reaction such as uranyl nitrate.[37] Products of various consistencies and solubilities are obtained, suitable for use in coating compositions, manufacture of safety glass, impregnation of paper or cloth, or in compositions for molding, etc.

Dreyfus[38] describes the polymerization of vinyl compounds containing hydrophile groups, as hydroxyl, carboxyl, sulfonic acid, amino or other acid or basic groups, which render them more readily soluble or dispersible in aqueous liquids. Vinyl chloride is heated to 80° to 100°C. in an autoclave with sodium glycol to produce glycolmonovinyl ether; this product may be polymerized by warming with benzoyl peroxide and under the radiation from a quartz mercury-vapor lamp. The polymerized product may be dissolved in water and used directly as a size.[39]

The polymerization of vinyl chloride by heating with a small proportion of benzoyl peroxide at about 50° to 60°C. for 24 hours may be assisted by a preliminary exposure of the initial material in the gaseous state to rays from a mercury lamp.[40] Voss and Dickhäuser[41] obtain products resembling celluloid by gradually heating a vinyl halide under pressure to a temperature preferably not above 100°C. The halide may be irradiated, and an inert or a polymerizable organic solvent, such as benzene or butadiene, and a catalyst such as benzoyl peroxide may be present.[42]

Shmidt states that the powdery product obtained by polymerization of vinyl chloride without a solvent is converted into a colorless, glass-like mass on prolonged exposure to the light of a quartz mercury arc.[43]

The polymerization of vinyl derivatives of phenols or cresols may be conducted in the presence of anhydrous aluminum chloride or ferric chloride as condensing agents by the action of ultraviolet light or heat.[44] Pressure polymerization is used in the preparation of resins from vinyl chloride by Waterman, Leendertse and Colthoff.[45] Although polyvinyl chloride has poor light stability,[46] glass laminated with a vinyl resin showed no discoloration after exposure for a thousand hours to the Uviarc or after two years in Florida.[47]

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[37] Carothers W. H., Berchet, G. J., and Jacobson, R. A., U. S. P. 1,963,074, June 19, 1934, to E. I. duPont de Nemours & Co.; *Chem. Abs.*, **28**, 4848 (1934).

[38] Dreyfus, H., British P. 398,173, Sept. 1, 1933; *Chem. Abs.*, **28**, 1360 (1934).

[39] Note also Zhukov, I., Komarov, V. A., and Sibiryakova, G. N., *Colloid J. (U.S.S.R.)*, **1**, 9 (1935) for bivinyl polymers. For the effects of light on the oxidation rates of 1,1,5,5-tetraphenyl-1,4-pentadiene and 1,1,6,6-tetraphenyl-1,5-hexadiene, see Bauer, K. H., and Herzog, H., *J. prakt. Chem.*, **147**, 4 (1936).

[40] Klatte, F., and Müller, H., U. S. P. 1,920,403, Aug. 1, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, **27**, 4816 (1933).

[41] Voss, A., and Dickhäuser, E., German P. 579,048, June 20, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, **27**, 4943 (1933); see also British P. 294,474, July 23, 1927, in which vinyl esters are polymerized under ultraviolet to make rubber substitutes, proteins, peptones or amino-acids being added to impart elasticity.

[42] British P. 385,004, Dec. 22, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, **27**, 4251 (1933).

[43] Shmidt, Y., *Org. Chem. Ind. (U.S.S.R.)*, **5**, 116 (1938); *Chem. Abs.*, **32**, 5957 (1938).

[44] British P. 409,132, April 26, 1934, to British Celanese, Ltd.; *Chem. Abs.*, **28**, 6158 (1934).

[45] Waterman, H. I., Leendertse, J. J., and Colthoff, P. J. G., *Chem. Weekblad*, **32**, 550 (1935); *Chem. Abs.*, **30**, 1147 (1936); Blackie, K. G., and Crozier, R. N., *Ind. Eng. Chem.*, **28**, 1155 (1936). See also Plauson, H., U. S. P. 2,127,135, Aug. 16, 1938; *Chem. Abs.*, **32**, 8043 (1938) for vinyl acetate polymerization by light when emulsified with sulfonated castor oil.

[46] Cuime, G. O., Jr., and Douglas, S. D., *Ind Eng. Chem.*, **28**, 1123 (1936).

[47] Sherts, J. H., and Fix, E. L., *Chem. Met. Eng.*, **43**, 177 (1936). Of a series of synthetic plastics tested for suitability for flexible windshield material for aircraft, cellulose acetobutyrate and vinyl acetate resins showed the greatest resistance to discoloration by ultraviolet light, but had certain disadvantages. Axilrod, B. M., and Kline, G. M., *J. Res. Bureau of Standards*, **19**, 367 (1937).

[48] Duggan, F. W., U. S. P. 2,126,179, Aug. 9, 1938; *Chem. Abs.*, **32**, 7610 (1938).

For stabilizing vinyl resins to light, Duggan uses one to five per cent of butyl salicylate or other phenol derivative with a single hydroxyl group and an alkyl-substituted carboxyl group ortho to the hydroxyl group.[48]

STEREOISOMERIC TRANSFORMATION

The *trans*-isomer has a greater ultraviolet absorption than the *cis*-form in many compounds, including: $ClCH{=}CHCl$, $C_2H_5CH{=}CHBr$, $CH_3CH{=}CHBr$, $ClCH{=}CHI$, and fumaric acid.[49]

The difference between the absorption curves of the geometrical isomers increases with decreasing wave-length. Compounds containing iodine differ in that this relation is inverted at wave-lengths greater than 3000A, the *cis* form absorbing more in this region than the *trans* form. The inversion may be due in some manner to the liberation of free iodine.[50]

According to van de Walle and Henne,[51] if either the *cis* or *trans* isomer of chloroiodoethylene is exposed to sunlight for one hour, the same equilibrium mixture (which contains 17.5 per cent of the *trans* form) is obtained. The theory underlying the conversion of geometrical isomers has been discussed by Olson [52] and by Mulliken,[53] and studies of the process were made in aqueous solutions of various fumaric and maleic acids by Olson and Hudson,[54] who reviewed the earlier experimental work. It is suggested that in the normal state the carbon atoms of the unsaturated compounds are to be regarded as two tetrahedra joined along a common edge. On excitation by light, they may be considered as joined only at one corner. Rotation about this corner with inversion of one of the carbon atoms will account for the occurrence of a transition between optical isomers if it occurs before a collision removes the energy of excitation and restores a normal state in which the double bond is present. Besides the theory of free rotation in the upper electronic state, Olson discussed the possibility of the addition of an atom or free radical to the face of the carbon tetrahedron, followed by the simultaneous ejection of another group accompanied by isomerization.[55]

The probability p that a molecule in an excited electronic state will return to the *trans* state on deactivation bears to the probability that it will yield the *cis* form (1-p) the ratio given by

$$\frac{p}{1-p} = \frac{C_{Tr}}{C_{Cis}} \times \frac{\epsilon_{Tr}}{\epsilon_{Cis}}$$

in which ϵ_{Tr} and ϵ_{Cis} are the extinction coefficients for the monochromatic light employed and C_{Tr} and C_{Cis} are the mole percentages of the *trans* and *cis* isomers. It was possible to test the relation in the gas state in the case of the isomers of dichloroethylene and dibromoethylene. Agreement with the theory was attained for the stationary states set up at various temperatures, the proportion of the two isomers present being determined by dielectric constant measurements. Further studies in the case of the chlorine compounds have been reported by Mahncke and Noyes.[56] There are three absorption regions: (1) continuous, by the carbon-chlorine bond from about 2500A with maxima at 1950A for the *cis* and 1850A for the *trans* form; (2) bands beginning at about 1540A, and (3) another continuous region extending down to 750A. In the first absorption region, produced by irradiation with an aluminum spark, atomic chlorine appears to be formed, with possibly some hydrogen chloride. For this reason, Olson's second theory is favored when the change is induced by light in this region of the spectrum. *cis*-Dichloroethylene also yields small amounts of a solid polymerization product, melting at 103.5° to 104°C. These observations have also been confirmed by Müller and Ehrmann.[57]

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[49] Errera, J., and Henri, V., *Compt. rend.*, **180**, 2049 (1925); **181**, 548 (1925). Errera, J., *J. phys. Radium*, **7**, 215 (1926).

[50] See also Kirrmann, A., and Volkringer, H., *Compt. rend.*, **182**, 1468 (1926); Ramart-Lucas, Mme., *Compt. rend.*, **188**, 638, 1301; **189**, 802 (1929); *Bull. soc. chim.*, **51**, 965 (1932); Bourguel, M., Gredy, B., and Piaux, L., *Compt. rend.*, **195**, 129 (1932).

[51] Van de Walle, H., and Henne, A., *Bull. sci. acad. roy. Belg.*, **11**, 360 (1925); *Chem. Abs.*, **20**, 1049 (1926).

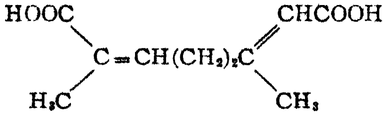
[52] Olson, A. R., *Trans. Faraday Soc.*, **27**, 69 (1931).

[53] Mulliken, R. S., *Phys. Rev.*, **41**, 751 (1932).

[54] Olson, A. R., and Hudson, F. L., *J. Am. Chem. Soc*, **55**, 1410 (1933).

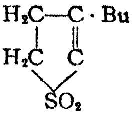
[55] Olson, A. R., *J. Chem. Physics*, **1**, 418 (1933).

The compound



undergoes a *cis-trans* isomerization in ultraviolet light to a more soluble form.[58]

Other Types of Isomerization. The isomerization of the sulfones of β-alkylbutadienes in alkaline solution under the influence of ultraviolet light consists in a displacement of the double linking in the ring toward the alkyl.[59] *Tert*-butylbutadienesulfone is isomerized to a compound



The isomer of the sulfone of 2-phenyl-1,3-butadiene and ozone when irradiated gave propiophenonesulfonic acid, showing that the change was not a *cis-trans* isomerism, as believed by Eigenberger[60] to occur in the irradiation of isoprene sulfone in the presence of alkali.

The homologs of isoprenesulfone isomerize on exposure to ultraviolet,[61] the change involving a wandering of the double bond.

According to Sherrill, Otto and Pickett,[62] sunlight and ultraviolet light of shorter wave-lengths transform 2-pentene into an isomeric form with slightly different physical properties. The transformed product adds hydrogen bromide to form 15 per cent of 3-bromopentane and 85 per cent of 2-bromopentane.[63] Birch and Stansfield[64] note that ultraviolet light favors the formation of a peroxide in cyclohexene.

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[56] Mahncke, H. E., and Noyes, W. A., Jr., *J. Chem Physics*, **3**, 536 (1935); *J. Am. Chem. Soc.*, **58**, 932 (1936).

[57] Müller, E., and Ehrmann, K., *Ber.*, **69B**, 2207 (1936). See also Stockmann, H., and Stoermer, R., [*Ber.*, **47**, 1793 (1914)] for work on γ-phenylvinylacetic acid in benzene solution

[58] Kuhn, R., Köhler, L., and Köhler, F., *Z physiol. Chem.*, **242**, 171 (1936)

[59] Backer, H. J., and Strating, J., *Rec trav. chim.*, **54**, 170, 618 (1935); *Chem. Abs.*, **29**, 2959 (1935); **30**, 3403 (1936).

[60] Eigenberger, E., *J. prakt. Chem.*, **129**, 312 (1931); *Chem. Abs.*, **25**, 2969 (1931); see also van Zuydewijn, E. de R., *Rec. trav. chim.*, **56**, 1047 (1937).

[61] Backer, H. J., and Strating, J., *Rec. trav. chim.*, **53**, 525 (1934); Backer, H. J., Strating, J., and Zuithoff, A. J., *Ibid.*, **55**, 761 (1936).

[62] Sherrill, M. L., Otto, B., and Pickett, L. W., *J. Am. Chem. Soc.*, **51**, 3032 (1929).

[63] For the ultraviolet absorption spectra of the various isomeric 2-pentenes, Carr, E. P., *J. Am. Chem. Soc.*, **51**, 3041 (1929).

[64] Birch, S. F., and Stansfield, R., *Nature*, **123**, 490 (1929).

Acetylene. The pure gas exhibits a banded absorption spectrum which begins at 2400A according to Kistiakowsky,[65] or at 2300A according to Hopfield,[66] or at lower pressures (less than 30 mm.) at 2070A.[67] A second system begins at about 1540A and at higher pressures a continuous absorption appears to set in at about 1880A, but may be due to an impurity.[68] Jonescu gives an extrapolated heat of dissociation of 204 kcal. Kato,[69] however, claims to have noted on the vaporization of solid acetylene at room temperatures, a broad continuous absorption spectrum and some series of bands with fine structure. The former, showing its strongest absorption at 2560 and 2400A, is held to indicate predissociation. The latter, appearing below 2500A, is attributed to deformation vibrations.

Berthelot and Gaudechon [70] found exposure of acetylene to the action of ultraviolet rays to bring about a partial polymerization to a yellow solid, but no decomposition. No benzene was found in these experiments.

Daylight or sunlight does not affect carefully purified and dried acetylene, but with wave-lengths less than 3000A, the reaction occurs at atmospheric or higher pressures and at room temperature, giving the yellow product without any separation of carbon.[71] The process is disturbed by the presence of oxygen or moisture, the latter leading to the formation of aldehyde. The wave-length limit was set at 2537A or less by Lind and Livingston,[72] who found the rate of polymerization to be proportional to the intensity of the absorbed light but independent otherwise of the acetylene pressure. The temperature coefficient was 1.25, and the quantum yield appeared to be 9.2 for the wave-length 2150A. This value was somewhat uncertain since measurements had to be limited to the beginning of the reaction owing to the deposition of the polymer on the walls of the vessel. The solid product, cuprene or a very similar substance, had the empirical formula $(C_{10}H_9)_n$. Some benzene formation was observed and could be accounted for by side reactions. Kato confirmed the formation of both cuprene and benzene by the wave-lengths 2103, 2100.5, 2065, 2036 and 2026A, but believed 2200A to produce chiefly benzene. At higher temperatures, 270° to 376°C., both he and Livingston and Schiflett [73] found benzene to predominate; the latter workers observed that two nonvolatile solids and a yellow, viscous, voltatile liquid were also produced. By following the absorption changes during the polymerization of acetylene, Kemula and Mrazek [74] detected the formation not only of benzene, but of naphthalene as well, together with less than 0.25 per cent of ethylene and ethane, but no hydrogen in the gas phase. Bates and Taylor [75] noted that polymerization could also be effected by excited mercury atoms, but that acetylene could not be hydrogenated by hydrogen which had been activated by excited mercury vapor.

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[65] Kistiakowsky, G. B., *Phys. Rev.*, **37**, 276 (1931).

[66] Hopfield, J. J., *Phys. Rev.*, **29**, 356 (1927).

[67] Herzberg, G., *Trans Faraday Soc.*, **27**, 379 (1931).

[68] For data on the classification of the bands, see Price, W. C., *Phys Rev*, **45**, 843 (1934); Jonescu, A., *Compt. rend.*, **199**, 710 (1934); Woo, S.-C., Liu, T.-K., Chu, T. C., and Chih, W., *J. Chem Phys.*, **6**, 240 (1938).

[69] Kato, S., *Bull. Inst. Phys.-Chem Research (Tokyo)*, **10**, 343 (1931); *Chem Abs.*, **25**, 5845 (1935).

[70] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1169 (1910); **151**, 395 (1910); **155**, 521 (1912).

[71] Reinicke, H., *Z. angew. Chem.*, **41**, 1144 (1928).

[72] Lind, S. C., and Livingston, R., *J. Am. Chem. Soc*, **52**, 4613 (1930); **54**, 94 (1932).

[73] Livingston, R., and Schiflett, C. H., *J. Phys. Chem.*, **38**, 377 (1934); see also Ch. Rosenblum, *Bull. soc. chim. Belg.*, **46**, 503 (1937); *Chem. Abs.*, **32**, 2840 (1938).

[74] Kemula, W., and Mrazek, S., *Z. physik Chem*, **23B**, 358 (1933).

[75] Bates, J. R., and Taylor, H. S., *J. Am. Chem. Soc.*, **49**, 2438 (1927).

Toul[76] believed polymerization in the presence of mercury vapor should not be considered a true photosensitization since it can still be observed when a source is used which does not emit the lines which excite mercury. The adddition of 0.006 per cent of oxygen did not affect the reaction. He also believed that an equilibrium was reached with the polymer after the volume had been reduced by 10 per cent, but this result could not be duplicated by Kemula.[77] Melville[78] treats the process as a sensitized chain reaction in which the excited mercury atoms form with the acetylene molecule a complex which successively builds up. The chain length is independent of the acetylene pressure, or surface, or of the rate at which the chains are started and may at 250°C. attain a maximum of 100. Cessation of growth is attributed to a special type of collision of the growing polymer with an acetylene molecule. Jungers and Taylor[79] found the rate of this photosensitized reaction to be 30 per cent greater with acetylene than with heavy-hydrogen acetylene. They gave the quantum yield as 6.5 for acetylene and 5 for acetylene-D_2.

Both methylacetylene and its double-bonded isomer allene can also be polymerized to white solids by ultraviolet radiation,[80] the quantum yields being 3.5 and 2.5, respectively. Diacetylene can also be polymerized.[81]

The photochemical oxidation of acetylene yields oxalic acid and a trace of aldehyde.[82] A mechanism was suggested by Mecke[83] according to which an excited acetylene molecule adds directly to an oxygen molecule. Livingston notes that further oxidation of the resulting glyoxal would account for the formation of the oxalic acid. It is also possible that two molecules of oxygen might be added to the excited acetylene molecule, the double peroxide then rearranging to oxalic acid. In the presence of water vapor in the gas phase in the absence of oxygen or in an aqueous solution, Livingston and Schiflett[84] could detect neither the formation of aldehydes nor ketones.

Heinemann[85] claims to secure the union of acetylene and methane by heating these gases or irradiating them with ultraviolet rays, in the presence of such catalytic metals as iron, nickel, copper, silver, iridium or platinum.

Carothers[86] finds the addition of thio-*p*-cresol to divinylacetylene $CH_2{=}CH{\equiv}CH{=}CH_2$ to be powerfully accelerated by the light of a mercury arc transmitted through soda-glass.

Polymerization of 1-chloro, 1-bromo- and 1-iodo-2-vinylacetylene to form resinous solids may be accelerated by the use of ultraviolet light, benzoyl peroxides, ozonides, etc. The iodine and bromine polymers are very explosive, and the chlorine derivative less so.[87]

Aldehydes and Ketones.[88] *Absorption.* These compounds in the gaseous state exhibit a broad absorption band attributed to the carbonyl group and having its maximum at about 2900 to 2800A.[89]

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[76] Toul, F., *Coll. Czech. Chem. Comm.*, **6**, 162 (1934); *Brit. Chem. Abs.*, **A**, 852 (1934).

[77] Kemula, W., *Coll. Czech. Chem. Comm.*, **7**, 319, 491, 493 (1935); *Chem. Abs.*, **29**, 7775 (1935); 30, 1644 (1936).

[78] Melville, H. W., *Trans. Faraday Soc.*, **32**, 258 (1936).

[79] Jungers, J. C., and Taylor, H. S., *J. Chem. Physics*, **3**, 338 (1935).

[80] Lind, S. C., and Livingston, R., *J. Am. Chem. Soc.*, **55**, 1036 (1933).

[81] Müller, F. G., and Banninger, A., *Helv. Chim. Acta*, **10**, 763 (1927).

[82] Livingston, R., *J. Am. Chem. Soc.*, **53**, 3909 (1931).

[83] Mecke, R., *Trans. Faraday Soc.*, **27**, 374 (1931).

[84] Livingston, R., and Schiflett, C. H., *J. Phys. Chem.*, **36**, 750 (1932).

[85] Heinemann, A., U. S. P. 1,202,385, Oct. 24, 1916; 1,134,667, Apr. 7, 1915.

[86] Carothers, W., *J. Am. Chem. Soc.*, **55**, 2008 (1933).

[87] Jacobson, R. A., U. S. P. 1,967,864, July 24, 1934; *Chem. Abs.*, **28**, 5834 (1934).

[88] For a recent review, see Leighton, P. A., *J. Phys. Chem.*, **42**, 749 (1938).

In hexane solutions, the absorption is in general similar. Formaldehyde, for example, either as vapor or in hexane at −70°, exhibits absorption chiefly between 3542 and 2750A, the maximum being at 2940A in hexane and at 2935A in the vapor.[90] Acetaldehyde and propionaldehyde behave similarly. Data on hexane solutions of higher aldehydes through octylaldehyde have been given by Conrad-Billroth.[91]

In water, however, the absorption of the three lowest aldehydes is somewhat displaced toward shorter wave-lengths, the maximum being at 2800A. The formation of hydrates also decreases the absorption. Choral hydrate lacks the typical aldehyde absorption band. The same is true of methylal and acetal.[92] Schou believes that in aqueous formaldehyde solutions there is less than one molecule of formaldehyde for 1200 molecules of the hydrated or polymerized form. Under certain conditions (the presence of a trace of alkali or after polymerization by acid) acetaldehyde gives spectral evidence that some of the molecules are present in enolic form.[93] This may be detected by a study of the absorption coefficients near the minimum close to 2400A. Herold and Wolf[94] find that propionaldehyde in water forms an association complex and a hydrate which do not absorb in the same region as the carbonyl group. In propyl alcohol as solvent, absorption measurements indicate that the greatest part of the aldehyde has been converted to the half-acetal.[95]

Interpretations of the absorption spectra of formaldehyde vapor have been given by Henri and Schou,[96] by Herzberg,[97] and by Dieke and Kistiakowsky.[98]

Observations in the far ultraviolet at 1750 to 1150A have been reported by Price.[99] About 32 bands are distinguished between 3550 and 2500A. Those on the longer wave-length side contain rotational fine structure but become diffuse, indicating predissociation, at about 2670A to 2750A. This limit is shifted toward the red at higher temperatures.

Reactions. Berthelot and Gaudechon[100] showed that ultraviolet light decomposes formaldehyde vapor with the production of carbon monoxide and hydrogen but no carbon dioxide. Some polymerization also occurred. Bredig and von Goldberger, however[101] claimed to have detected small amounts of carbon dioxide and methane, but Norrish and Kirkbride[102] were unable to verify these results. They show from the nature of the products and from energetic considerations that, although the light is absorbed by the carbonyl group, the primary dissociation does not yield a CH_2 group and an oxygen atom. Instead, CO is thought to be removed bodily, the hydrogen atoms combining without first separating from the molecule.

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[89] Purvis, J. E., and McCleland, N. P., *J. Chem Soc*, **103**, 433 (1913); Bielecki, J, and Henri, V., *Ber.*, **45**, 2819 (1912); Purvis, J. E., *J. Chem. Soc.*, **127**, 9 (1925), Eastwood, E, and Snow, C. P., *Nature*, **133**, 908 (1934).

[90] Schou, S. A., *Compt. rend.*, **186**, 690 (1928).

[91] Conrad-Billroth, H., *Z. physik. Chem.*, **B23**, 315 (1933).

[92] Schou, S. A., *Compt. rend.*, **182**, 965 (1926); *J. chim. phys.*, **26**, 69 (1929).

[93] See also Kwiecinski, L., and Marchlewski, L., *Bull soc. chim*, **45**, 591 (1929).

[94] Herold, W., and Wolf, K. L., *Z. physik Chem.*, **B12**, 165 (1931); *Z. Elektrochem*, **39**, 566 (1933).

[95] See also Backès, M., *Compt. rend.*, **200**, 1669 (1935).

[96] Henri, V., and Schou, S. A., *Nature*, **118**, 225 (1926); *Z. Physik*, **49**, 774 (1928); *J. chim. phys.*, **25**, 665 (1928); *Compt. rend.*, **182**, 1612 (1926); **186**, 1050 (1928); **199**, 849 (1934).

[97] Herzberg, G., *Trans. Faraday Soc.*, **27**, 378 (1931).

[98] Dieke, G. H., and Kistiakowsky, G. B., *Phys. Rev.*, **45**, 4 (1934); *Proc Nat. Acad. Sci.*, **18**, 367 (1932). See also Kato, S., *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **23**, 256 (1934), *Chem Abs.*, **28**, 4312 (1934).

[99] Price, W. C., *Phys. Rev.*, **46**, 529 (1934).

[100] Berthelot, D., and Gaudechon, H, *Compt. rend.*, **151**, 478 (1910).

[101] Bredig, G., and von Goldberger, A., *Z. physik. Chem.*, **110**, 521 (1924); see also Frank, A, and Pollitzer, E., *Monatsh.*, **34**, 797 (1913).

[102] Norrish, R. G. W., and Kirkbride, F. W., *J. Chem. Soc.*, **135**, 1518 (1932); *Trans. Faraday Soc.*, **27**, 404 (1931).

$$\begin{matrix}H\\H\end{matrix}>CO + h\nu \longrightarrow H_2 + CO$$

This view was based upon what was then known of the behavior of other aldehydes and ketones. If ketones with two different alkyl groups should produce free radicals in the primary process, a mixture of hydrocarbons might be expected as a result of the photochemical decomposition. Actually, it appeared that only one hydrocarbon resulted. Should a free methyl radical be produced from acetaldehyde in the primary process, one might expect ethane as well as methane. This was not observed. Furthermore, a primary process involving free radicals might give rise to a short chain reaction, the free radicals reacting with an additional molecule of the original aldehyde or ketone. Bowen and Watts[103] did, indeed, find a quantum yield of two for the decomposition of acetaldehyde, but it seemed that the occurrence of a complicating polymerization made these results not very accurate. Norrish and Kirkbride therefore proposed as a general mechanism for the primary process in the decomposition of aldehydes and ketones, the elimination of CO, the remaining radicals combining without first separating from the molecule. Subsequent work has shown, however, that other processes must also be admitted. See, for example, the discussion of acetone.

The formaldehyde decomposition can be made to proceed by wave-lengths corresponding to the region of rotational fine structure, that is, by wave-lengths longer than those which cause predissociation. The quantum yield was 1.1 at 3030 to 3130A or 0.7 at 3340 to 3650A In the predissociation region the quantum yield was 0.9 (2540-2650A).

Later, Patat[104] found that the addition of oxygen produced no change in the ratio of hydrogen to carbon monoxide produced by irradiating formaldehyde vapor within the fine structure region longer than 3000A and uncomplicated by an underlying continuum. From this it was concluded[105] that no hydrogen atoms are there produced. Patat showed the same to be true of the reaction conducted in part of the predissociation region (3000-2700A), thus supporting the Norrish mechanism. The presence of free hydrogen atoms could, however, be detected by this method when the irradiation was made in the region of continuous absorption.

The primary process advanced by Mecke[106] and by Herzberg[107] involved a dissociation in the predissociation region into H and HCO. This was assumed to require 92 kcal., the energy of the 2750A line being 105 kcal. Norrish and Patat each gave reasons for believing that this is not the actual process at the longer-wave portions of the predissociation region. Patat suggests that molecular thermal vibrations may contribute part of the energy required for the simultaneous breaking of two C—H bonds, which must occur since hydrogen atoms are not detected.

Experiments by Norrish and Noyes with radiations in the Schumann region gave no evidence for the formation of oxygen atoms and CH_2 in the primary process, due probably to wave-lengths shorter than 1600A. The final products were the same as those produced by longer wave-lengths in the near ultraviolet.[108]

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[103] Bowen, E. J., and Watts, H. G., *J. Chem. Soc.*, **129**, 1607 (1926).

[104] Patat, F., *Z. physik. Chem.*, **25B**, 208 (1934).

[105] Patat, F., and Löcker, T., *Z. physik. Chem.*, **27B**, 431 (1934).

[106] Mecke, R., *Nature*, **125**, 526 (1930).

[107] Herzberg, G., *Trans. Faraday Soc.*, **27**, 383 (1931).

[108] Norrish, R. G. W., and Noyes, W. A., Jr., *Proc. Roy. Soc.*, **A163**, 221 (1937).

Before considering the photolysis of other aldehydes, a few other reactions of formaldehyde may be briefly mentioned. Ghosh and Nandy[109] found its oxidation by hydrogen peroxide in acid solution with a tungstic acid sol as photosensitizer, to be unimolecular with respect to hydrogen peroxide at low concentrations. It tended to become of zero order at higher ones. For low concentrations of free hydrochloric acid, the velocity coefficient varies as the square root of the intensity of the incident radiation, but the variation of the velocity with the intensity of the light is much less at higher acid concentrations. The quantum efficiency of the reaction is between two and seven.

In a reaction between chlorine and formaldehyde, the final products are carbon monoxide and hydrogen chloride. By an analysis of the curves giving the change of pressure with time of irradiation, Krauskopf and Rollefson,[110] who used mixtures of the reactants in various proportions, concluded two reactions to be involved. The first, a very rapid reaction, involved the formation of a new intermediate compound, formyl chloride, produced together with hydrogen chloride by the action of chlorine atoms, formed in the primary photochemical process, upon formaldehyde. This then reacted more slowly in a secondary reaction, which might be either a thermal or a sensitized photochemical reaction, to yield carbon monoxide and hydrogen chloride. This decomposition appeared to be a heterogeneous surface reaction. Under certain conditions, the first reaction proceeded with explosive rapidity. The overall reaction had a quantum yield of about 10^4, and was very susceptible to the action of such inhibitors as oxygen or mercuric chloride. Side reactions, such as the polymerization or decomposition of formaldehyde, the formation of phosgene, or one between hydrogen chloride and formaldehyde, were so slow as to be negligible.

Roman[111] claims to convert such aldehydes as formaldehyde into alcohols by the action of luminous energy from which harmful radiations have been filtered.

Acetaldehyde. Acetaldehyde is also partly polymerized and partly decomposed into methane and carbon monoxide in ultraviolet light,[112] even that of sunlight. In some experiments of Berthelot and Gaudechon particularly with extreme ultraviolet rays, it was observed that the proportion of methane to carbon monoxide was somewhat less than exactly that corresponding to a simple decomposition. This was assumed to be due to a polymerization of the acetaldehyde in part to paraldehyde which was then photolyzed to carbon monoxide and ethane or more complex substances. Radiations of wave-length 2500A caused a rapid polymerization, both paraldehyde and metaldehyde being formed. The presence of water checked these processes, but favored the formation of formic acid. It was also believed that even in the absence of oxygen, a portion of the aldehyde was oxidized to acetic acid.

By comparison with a uranyl oxalate actinometer the quantum yield of which was taken as one, Bowen and Watts[113] concluded that in the unsaturated vapor of acetaldehyde, the quantum yield for polymerization is 1.6 and for decomposition 0.4. The use of the more accurate value of 0.55 for the quantum yield of the actinometer found by Leighton and Forbes[114] makes these values 0.88 and 0.22, respectively.

The absorption of acetaldehyde extends from about 3480 to 2300A, with a maximum at about 2890A, the absorption falling off on either side, according to Smith.[115] Bands with distinct rotational structure set in faintly at 3484A and extend to about 3300A, below which the structure gradually becomes more diffuse and disappears because of predissociation near 3080A. From this wave-length, however,

[109] Ghosh, J. C., and Nandy, S. K., *J. Indian Chem. Soc.*, **6**, 975 (1929); *Chem. Abs.*, **24**, 2055 (1930).

[110] Krauskopf, K. B., and Rollefson, G. K., *J. Am. Chem. Soc.*, **56**, 2542 (1934).

[111] Roman, L. H., French P. 734,065, July 19, 1930; *Chem. Abs.*, **27**, 992 (1933).

[112] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **156**, 68, 233 (1913).

[113] Bowen, E. J., and Watts, H. G., *J. Chem. Soc.*, 1607 (1926).

[114] Leighton, W., and Forbes, G. S., *J. Am. Chem. Soc.*, **52**, 3139 (1930).

[115] Smith, J. H. C., *Carnegie Inst. Reports*, **27**, 178 (1928).

about 60 diffuse bands continue to 2820A.[116] According to Leighton and Blacet [117] these diffuse bands extend even further to 2730A, and traces can be detected even at 2660A. There is also, underlying the banded absorption, a broad continuous absorption, which begins at about 3080, that is, in the region where the bands still show some rotational fine structure; it has a maximum at 2750A. The greatest total absorption (bands plus continuum) occurs at 1890A.[118]

Using the total radiation from a mercury arc, Smith [119] found the rate of the decomposition of acetaldehyde vapor to be independent of pressure and directly proportional to the intensity of the incident light. That of polymerization was directly proportional to pressure and proportional to the logarithm of the light intensity. Smith found that decomposition is produced chiefly by the shorter wave-lengths, and that polymerization could be produced throughout the absorption band with an estimated quantum yield of only 0.04 for an average wave-length of 2650A.

Leighton and Blacet in general confirmed the observations of Smith on the relative predominance of the two types of reactions at various wave-length regions by careful studies of the quantum yields of each at several pressures in the fine structure, predissociation and predominantly continuous regions. Fluorescence of the aldehyde vapor could be observed between 3342 and 2804A, but not at shorter wave-lengths. Because of this, it was suggested that a mechanism involving activated molecules must apply in these regions and be concerned with polymerization. It was found that the yield for the polymerization reaction at a pressure of 200 mm. dropped from 0.47 at 3130A to only 0.1 at 2537A in the region of continuous absorption. Conversely, the yields for decomposition were 0.2 and 0.9 under these conditions. At 3130A there is considerable fluorescence, the bands are not altogether without fine structure and the amount of continuous absorption is small. Here the yield of polymerization increases with the pressure from 0.266 at 14 mm. to 0.638 at 291 mm. The yield for decomposition decreases from 0.396 at 14 mm. to 0.193 at 291 mm. This decrease was attributed to a removal of activated molecules, which were believed also to contribute to the process of dissociation. The mechanism suggested for the observations in this wave-length region were analogous to those of Norrish for the decomposition of formaldehyde in its long wave-length region.

$$\mathrm{RCHO} + h\nu \longrightarrow \mathrm{RCHO}^*$$
$$\mathrm{RCHO}^* + \mathrm{RCHO} \longrightarrow (\mathrm{RHCO})_2, \text{ etc. for polymerization.}$$
$$\mathrm{RHCO}^* \longrightarrow \mathrm{RHCO} + h\nu' \text{ (fluorescence.)}$$
$$\mathrm{RCHO}^* + \mathrm{M} \longrightarrow \mathrm{RHCO} + \mathrm{M(K.E.)}, \text{(deactivating collisions)}$$
$$\mathrm{RHCO}^* + \mathrm{M} \longrightarrow \mathrm{RH} + \mathrm{CO} + \mathrm{M}. \text{ (decomposition.)}$$

In the region of pure continuous absorption below 2730A where the quantum yield of decomposition approaches unity, increasing the pressure had almost no effect on the yield. In this region, where there was no fluorescence, as well as in the diffuse predissociation bands, a decomposition mechanism was suggested as had been proposed by Herzberg. It differed from that of Norrish in assuming the presence of free radicals.

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[116] Schou, S. A., and Henri, V., *Z. Physik*, **49**, 774 (1928); Henri, V., *Trans. Faraday Soc.*, **25**, 765 (1929); Schou, S. A., *J. chim. phys.*, **26**, 1 (1929).

[117] Leighton, P. A., and Blacet, F. E., *J. Am. Chem. Soc.*, **55**, 1766 (1933).

[118] For the influence of acids and alkalies upon the absorption spectra of aqueous solutions altering the amount of an enolic form, see Schou, S. A., *Compt. rend.*, **184**, 1452 (1927) and Fromageot, C., *J. chim. phys.*, **24**, 623 (1927).

[119] Smith, J. H. C., *loc. cit.*

$$\begin{aligned}
&\mathrm{RHCO} + h\nu \longrightarrow \mathrm{R} + \mathrm{HCO}\\
&\mathrm{R} + \mathrm{HCO} \longrightarrow \mathrm{RH} + \mathrm{CO}\\
&\mathrm{R} + \mathrm{R} + \mathrm{M} \longrightarrow \mathrm{R_2} + \mathrm{M}\\
&\mathrm{HCO} + \mathrm{HCO} \longrightarrow \mathrm{H_2} + 2\mathrm{CO}\\
&\mathrm{R} + \mathrm{HCO} + \mathrm{M} \longrightarrow \mathrm{RHCO} + \mathrm{M}.
\end{aligned}$$

That some polymerization (yield 0.1) could still be observed at these wave-lengths suggested the possibility that the free radicals could induce polymerization in other molecules through the formation of intermediate compounds.

Particularly interesting results were obtained with the wave-length 3342A which lies between two band maxima, so that the absorption is ascribed principally to the weak underlying continuum. The result was a high quantum yield for decomposition as in the short wave-length regions (0.72-0.82) and little or no polymerization. This observation and the gradual changes in the quantum yields of the two processes, with no sharp breaks, agreed with the gradual transition observed between the different absorption regions. The maximum probability of excitation to the upper electronic state which leads to dissociation occurs at about 3100A, very close to the point at which all rotational structure disappears from the bands.

The chief support advanced for the proposed dissociation mechanism was the subsequent[120] finding of hydrogen in the decomposition products by a new method of microanalysis,[121] although Leighton and Blacet had been unable to detect it in their original work. From the ratios of hydrogen to carbon monoxide found at three wave-lengths, (0.05 at 3130A, 0.10 at 2804A and 0.155 at 2537A), it was concluded that the fraction of the molecules yielding hydrogen increases linearly from 10 per cent at 3130 to 31 per cent at 2537A. These observations made at 300 mm. favored a short-chain reaction at room temperatures.

Leermakers[122] found that at temperatures above 80°C., and with irradiation of acetaldehyde by 3130A, the short-chain reactions leading to the production of hydrogen were replaced by or accompanied by longer chains leading to the production of methane along with carbon monoxide. The rate of the chain reaction was proportional to the concentration of the aldehyde and to the square root of the light intensity. Below temperatures of 160°C., a term, 0.3 *I*, had to be added to the rate equation to cover that photolysis which was not a part of the chain reaction. The quantum yield increased enormously with the temperature reaching 310 at 309.5°C., when light of low intensity was used. In the case of formaldehyde, Leermakers also found a chain length of 100 at temperatures between 100° and 400°C. On the other hand, the acetone decomposition is not similarly affected, the quantum yield remaining at 0.76 at high temperatures. He suggests that acetone may follow the Norrish type of primary process, although acetaldehyde exhibits a chain mechanism involving methyl radicals. The energy of activation for the reaction: $CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$ is 9.8 kcal. and that of the formaldehyde reaction $H + HCHO \rightarrow H_2 + HCO$ is 16.2 kcal. Patat[123] uses the para-hydrogen conversion method for calculating the free radical concentrations. Blacet and Volman now believe the Leermakers chain mechanism for the reaction at high temperature applies also at room temperatures.

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[120] Blacet, F. E., and Roof, J. G., *J. Am. Chem. Soc.*, **58**, 278 (1936); Blacet, F. E., and Volman, D., *Ibid.*, **60**, 1243 (1938).

[121] Blacet, F. E., and MacDonald, G. D., *Ind. Eng. Chem., Anal. Ed.*, **6**, 334 (1934). Compare Franke, A., and Pollitzer, E., *Monatsh.*, **34**, 797 (1913)

[122] Leermakers, J. A., *J. Am. Chem. Soc.*, **56**, 1537 (1934)

[123] Patat, F., *Naturwiss.*, **24**, 62 (1936); *Z. physik. Chem.*, **32B**, 274 (1936).

Pearson[124] failed to detect free radicals in the primary products of the photolysis of acetaldehyde and of propionaldehyde (as well as methylbutyl ketone) by their action on metallic mirrors, although they could be detected in the case of acetone, methyl ethyl ketone and diethyl ketone. Later, however, Pearson and Purcell[125] succeeded in demonstrating the presence of free radicals in the case of acetaldehyde and attributed previous failures to the presence of a thin film of polymerized aldehyde upon the mirrors. Since, when equal quantities of acetaldehyde and acetone were irradiated, six times as many free radicals were found as when the aldehyde alone was used, it was suggested that there may be some underlying difference in the mechanisms of the photolyses of aldehydes and ketones, although it was concluded that free radicals must be admitted, as Leighton and Blacet maintained, to play some part in the photolysis of aldehydes. Glazebrook and Pearson,[126] who have measured the relative quantities of free radicals formed by the dissociation of a number of ketones, state that in the case of acetone, the acetyl and methyl radicals are formed in comparable quantities. The former, however, rapidly combine with one another to form diacetyl, and have a short life, possibly dissociating further into a methyl radical and carbon monoxide.

It was earlier claimed by Ghosh and Nandy[127] that the decomposition in dilute aqueous solutions involves a chain reaction, since the quantum yield is 13.4. They found the reaction to be unimolecular, the velocity coefficient being independent of the initial concentration. There was a small but definite temperature coefficient.

Discherl[128] states that acetoin, $CH_3CH(OH)COCH_3$, is formed when aqueous solutions of acetaldehyde or of pyruvic acid are irradiated by ultraviolet light, but the mechanism is not clear. A quartz apparatus designed for carrying out this reaction has been described by Benson and Cadenhead.[129]

The action of ultraviolet light on trimethylacetaldehyde was shown by Hinterberger[130] to cause the evolution of carbon monoxide. Conant, Webb and Mendum isolated isobutane from a sample of this compound allowed to decompose for many weeks in daylight in the absence of oxygen. By filter experiments, it was shown that light in the range 2950 to 3200A was effective. The addition of a small amount of hydroquinone decreased the decomposition to a third. Similar results were also obtained with dimethylacetaldehyde. Ultraviolet light also accelerated autoxidation of the trisubstituted aldehyde.

In the case of propionaldehyde, Leighton and Blacet[131] reported results very similar to those for acetaldehyde. They indicated their belief that there may be two distinct primary processes, one of which occurring to the extent of 80 per cent or more yields directly RH and CO, as postulated by Norrish. The other yields R_2, hydrogen (which could be detected), and carbon monoxide. They also extended their work to include *n*- and *iso*-butyraldehyde.[132]

The quantum yields in the case of acetaldehyde and propionaldehyde are greatly reduced in the presence of small amounts of nitric oxide.[183] The photochemical decomposition of isovaleraldehyde involves two types of reactions, according to Norrish and Bamford.[184] One, in line with the usual Norrish mechanism, yields directly CO and isobutane and occurs to the extent of 47 per cent. The other, a new type of dissociation, gives rise to propylene and acetaldehyde, which then suffer further decomposition. In this case there is a rupture between the α and β carbon atoms of the hydrocarbon chain, producing an olefin and a simpler aldehyde. This type of reaction has been found to occur more readily in ketones than in aldehydes and is said to be facilitated by extending the length of the hydrocarbon chain.[185]

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[124] Pearson, T. G., *J. Chem. Soc.*, 1718 (1934).

[125] Pearson, T. G., and Purcell, R. H., *J. Chem. Soc.*, 1151 (1935); 253 (1936); Glazebrook, H. H., and Pearson, T. G., *Ibid.*, 1777.

[126] Glazebrook, H. H., and Pearson, T. G., *J. Chem. Soc.*, 567 (1937).

[127] Ghosh, J. C., and Nandy, S. K., *J. Indian Chem. Soc.*, **6**, 911 (1929); *Brit. Chem. Abs.*, **1930A**, 555.

[128] Discherl, W., *Z. physiol. Chem.*, **188**, 225 (1930).

[129] Benson, G., and Cadenhead, A., *J. Soc. Chem. Ind.*, **54**, 40 (1934).

[130] Hinterberger, H., Dissertation, Vienna, 1923; cited by Conant, J. B., Webb, C. N., and Mendum, W. C., *J. Am. Chem. Soc.*, **51**, 1248 (1929).

[131] Leighton, P. A., and Blacet, F. E., *J. Am. Chem. Soc.*, **54**, 3165 (1932).

[132] Leighton, P. A., and Blacet, F. E., *J. Am. Chem. Soc.*, **54**, 3165 (1932); **55**, 1766 (1933).

Oxidation of Aldehydes. It has been claimed that per-acids may be obtained by treating aldehydes with oxygen, under the influence of chemically active rays.[186] Taylor and Gould[137] found the photoöxidation of aqueous formaldehyde solutions to be a chain reaction. According to Carruthers and Norrish,[188] the process is

$$HCHO + 1/2O_2 \longrightarrow HCOOH.$$

Part of the formic acid decomposes to water and carbon monoxide and part to hydrogen and carbon dioxide. 45 per cent of the formaldehyde yields formic acid, 20 per cent water and carbon monoxide, 3 per cent carbon dioxide and hydrogen, 32 per cent is polymerized and a slight amount is photolyzed. The latter process may be reduced by the presence of a trace of iodine vapor.

Acetaldehyde yields 59 per cent oxygen, 25 per cent carbon monoxide, 1.5 per cent ethylene, 4 per cent methane and a trace of hydrogen. The condensed products give the reactions of peroxides, and the compound $CH_3CO.O.O.COCH_3$ may be an intermediate product. The quantum efficiency of the process in the wave-length region 2480 to 2750A is 11 moles decomposed per quantum absorbed. (It is ten in the case of formaldehyde.) In the presence of nitrogen, the quantum efficiency for the formation of biacetyl is approximately 22. The formation of an intermediate peracetic acid had been postulated by Bowen and Tietz[139] who regarded it as the first step of a chain reaction. Its reaction with a molecule of acetaldehyde gives acetic acid, the formation of which had been noted by Bertholet and Gaudechon. On the other hand, its reaction with a second molecule of peracetic acid gives the comparatively stable intermediate peroxide the formula of which was given above. The rate of the reaction is, according to Bowen and Tietz, independent of the oxygen concentration and proportional to the acetaldehyde concentration and to the square root of the light intensity. It is essentially the same at various wave-lengths within the absorption band of the aldehyde. In hexane solutions, alcohol acts as an inhibitor and the reaction becomes directly proportional to the light intensity.

Further evidence for the chain nature of the oxidation of aldehydes both in light and darkness has been given by Bäckström,[140] who investigated particularly benzaldehyde and enanthaldehyde. The maximum yields amounted to about 10,000 for the former and 15,000 for the latter. He has also shown that the ketone-sensitized oxidation[141] of aldehydes has the same chain mechanism as the photochemical oxidation:

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[183] Mitchell, J. W., and Hinshelwood, C. N., *Proc. Roy. Soc.*, **159A**, 32 (1937).

[184] Norrish, R. G. W., and Bamford, C. H., *J. Chem. Soc.*, 1504 (1935).

[185] For the behavior of normal and isobutyraldehydes which, in the main, resemble acetaldehyde, see Leighton, P. A., Levanas, L. D., Blacet, F. E., and Rowe, R. D., *J. Am. Chem. Soc.*, **59**, 1843 (1937).

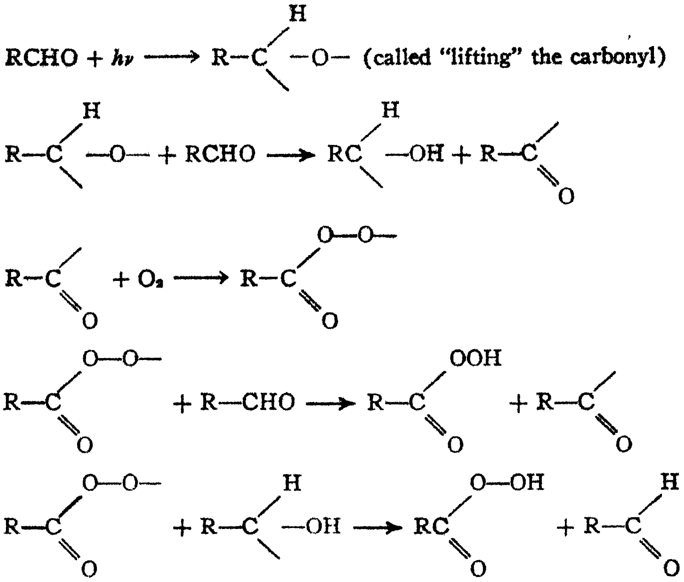
[186] Consortium für Elektrochemische Industrie, British Patent 16,849, July 22, 1913.

[187] Taylor, H. S., and Gould, A. J., *J. Phys. Chem.*, **37**, 367 (1933).

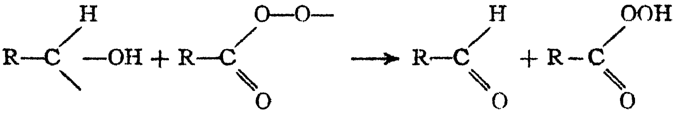
[188] Carruthers, J. E., and Norrish, R. G. W., *J. Chem. Soc.*, 1036 (1936).

[189] Bowen, E. J., and Tietz, E. L., *J. Chem. Soc.*, 23 (1930); see also Cantieni, R., *Z. wiss. Phot.*, **36**, 119 (1937) for the formation of a peroxide during the irradiation of paracetaldehyde in oxygen.

[140] Bäckström, H., *J. Am. Chem. Soc.*, **49**, 1460 (1927).


(called "lifting" the carbonyl)

The chains are broken by the mechanism:



This mechanism was believed to be in agreement with the rates found by Bowen and Tietz in the case of gaseous acetaldehyde.

Bogert and McDonough[142] have studied the rates of autoxidation of seventeen aldehydes used in perfumery. With the exception of salicylaldehyde, they are subject to autoxidation in daylight and in darkness, the daylight rates being, except in the case of the cinnamaldehyde types, considerably greater than those in darkness. The temperature coefficients were the same for both the light and dark reactions.

Unsaturated Aldehydes. Acrolein is unaffected by diffused daylight in two months when exposed in sealed tubes, but sunlight solidifies about one-third of it in quartz tubes in twelve days and the mercury arc completely solidifies it in 1½ hours.[143]

Thompson and Linnett[144] have found its absorption spectrum to consist of two widely separated regions. Between 3800 and 2900A there are bands with fine rotational structure, at least at the long-wave end, and no underlying continuum. No fluorescence, however, could be observed on irradiation within this region, but polymerization occurred. The maximum absorption was found at 3450A. The bands in the second absorption region beginning at 2350A were narrow and diffuse and probably accompanied by a continuum, at least at the shorter wave-lengths. Recently, Eastwood and Snow[145] have given detailed analyses of the spectrum of this and other aldehydes, including some saturated ones. Blacet, Fielding and Roof[146] state that in the region of sharp bands (3660-3130A) the quantum yield for polymerization is less than 0.5. At 3020A where the absorption is very diffuse, it is 1.0. On the border between banded and continuous absorption (2804A) it is 10, and in the continuous region at 2654-2537A, it is 19. Free radicals are assumed to play a part in the mechanism. There is an induction period. Irradiation also produces small quantities of acetylene but the quantum yield for dissociation is low, about 0.01 at 3665A.

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[141] Backström, H., *Z. physik. Chem.*, B25, 99 (1934).

[142] Bogert, M. T., and McDonough, E. G., *Drug and Cosmetic Ind.*, 32, 312, 332, 514, 533, 536, 538, 540 (1933); *Chem. Abs.*, 27, 4625 (1933).

[143] Moureu, C., Murat, M., and Tampier, L., *Ann. chim.*, 15, 221 (1921); *Compt. rend.*, 171, 1267 (1921); *Chem. Abs.*, 15, 2220 (1921); 16, 55 (1922); Moureu, C., Dufraisse, C., and Badoche, M., *Bull. soc. chim.*, 35, 1572, 1591 (1924) have also investigated its oxidation in light.

[144] Thompson, H. W., and Linnett, J. W., *Nature*, 134, 937 (1934); *J. Chem. Soc.*, 1452 (1935).

Sigmund[147] held the theory that the presence of a carbon-to-carbon double bond, or a phenyl group, or of both together in an aldehyde molecule, stabilizes the carbonyl group, presumably in some manner by "partial valences." After saturation, the carbonyl group can be split off in the usual manner by the action of ultraviolet rays. Thus, hexahydrophenylacetaldehyde split off gas containing 80 per cent of carbon monoxide and hexahydrotoluene could be isolated. Hexahydro-β-phenylpropionaldehyde also eliminated carbon monoxide but at a lower rate. The residue consisted of higher polymerization products of the aldehyde, the trimer being isolated. Dodecylaldehyde gave a gas containing 80 per cent of carbon monoxide and in the residue $C_{11}H_{24}$ was identified.[148]

A similar inertness has been found by Blacet and Roof[149] in crotonaldehyde which has an absorption spectrum resembling that of acetaldehyde shifted toward the red by several hundred A. It has discrete bands beginning at 3800A and continuing to 3245A where the bands begin to fade. From 3090 to approximately 2600A the absorption is apparently continuous. At 2550A a second region of continuous absorption begins and extends into the Schumann region. It is attributed to an electronic transition in the hydrocarbon end of the molecules. At 3660A only one quantum out of 150 was effective in causing a reaction, probably a polymerization. The wave-lengths 3130, 3020, 2804, 2654, 2537 and 2399A, all but the first of which are in regions of apparently continuous absorption, caused no detectable decomposition. Similar results were obtained when the aldehyde was subjected to the action of excited mercury atoms, but in the presence of oxygen a photochemical oxidation of the aldehyde vapors occurred.

Two explanations of this inertness in a region indicative of dissociation were suggested. The first, which relates the stability in some manner to the presence of conjugated double bonds, assumed that the absorption might be only apparently continuous, the energy of excitation being rapidly dissipated in other modes of vibration than that of the carbonyl group responsible for the absorption. More acceptable, however, would be the view that the continuous region implies, as usual, a true dissociation, but that this is followed by a rapid recombination. The need for the occurrence of three-body collisions may decrease in the case of such a complex molecule, the excess energy going into some kind of excitation. This was believed to be in line with the fact that the quantum yields for decomposition of the higher saturated aldehydes are less than unity in the continuous absorption region, decreasing with increase in the molecular weight.

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[145] Eastwood, E., and Snow, C. P., *Proc. Roy. Soc.*, **149A**, 434, 446 (1935).

[146] Blacet, F. E., Fielding, G. H., and Roof, J. G., *J. Am. Chem. Soc.*, **59**, 2375 (1937).

[147] Sigmund, F., *Monatsh.*, **52**, 185 (1929).

[148] Müller, A., *Seifensieder-Ztg.*, **63**, 441 (1936); *Chem. Abs.*, **30**, 7556 (1936), notes a polymerization of phenylacetaldehyde in sunlight.

[149] Blacet, F. E., and Roof, J. G., *J. Am. Chem. Soc.*, **58**, 73, 608 (1936).

To summarize the reactions of the aldehydes,[150] it may be stated that some on activation dissociate to yield carbon monoxide and hydrocarbons, although a certain percentage of the molecules appear to dissociate to give free radicals.[151] Furthermore, in the gas phase, the simpler aldehydes and ketones produce carbon monoxide and hydrocarbons, but the more complicated members tend to dissociate to yield simpler aldehydes or ketones and unsaturated hydrocarbons. Unsaturated aldehydes such as acrolein or crotonaldehyde are relatively inert.[152] Recently, a number of aldehydes have been studied in aqueous solution by Farkas and Hirschberg.[153] The quantum yields for molecules destroyed are: formaldehyde, 0.5; acetaldehyde, 2.5; propionaldehyde, 1.8; crotonaldehyde, much less than one. In the case of acetaldehyde, acetaldol is formed; the formation of an aldehyde molecule with free valences may be the primary process.

Ketones. Berthelot and Gaudechon[154] found acetone to be rapidly decomposed by ultraviolet light, the gas formed having 49 per cent carbon monoxide, 46 per cent ethane and but 5 per cent methane. In aqueous solutions, carbon dioxide was also formed. With sunlight and air, acetic acid was also formed.[155]

Henri and Wurmser[156] definitely showed the reaction to be related to the ultraviolet absorption spectrum of the carbonyl group.[157]

At first it was believed[158] that absorption in the region about the maximum was continuous, Noyes[159] stating that no fine structure or discontinuities had been reported in the absorption curve even when long path-lengths of acetone vapor at low pressures were studied. He believed it an open question as to whether it is justifiable to assume that this implies a primary dissociation process in analogy with the continuous spectra of diatomic gases, since in such complex molecules reasonance effects might lead to an overlapping of energy levels sufficient to preclude the appearance of any very marked banded structure. Noyes preferred to regard the primary process as of the type of predissociation by collision. More recently, however, Bowen and Thompson[160] using long columns of acetone vapor at pressures of 0.5 to a few millimeters detected four groups of bands each composed of about 25 diffuse bands. Their centers were at 3150, 2900, 2710, and 2570A. At higher pressures (up to about 200 mm.) the bands widened to produce a region of continuous absorption extending from 3200 to 2400A, with its maximum at 2800A, characteristic of compounds containing the carbonyl group. They discarded the hypothesis that predissociation splits a carbon-hydrogen or carbon-carbon bond, and attributed the diffuseness of the bands merely to an unresolved close packing of rotation lines, which they believed similar to that in the spectra of other Y-shaped molecules.

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[150] Rollefson, G. K., *J. Phys. Chem*, **41**, 259 (1937).

[151] See, however, Norrish, R. G. W., and Bamford, C. H., *Nature*, **140**, 195 (1937). They also investigate the reactions in liquid paraffin solution at 100°, the products consisting of CO, RH and R'H, the latter being produced by dehydrogenation of the solvent by the alkyl radicals.

[152] It has been observed by Kuhn, R., Badstubner, W., and Grundmann, C., [*Ber.*, **69B**, 98 (1936)] that pure crotonaldehyde does not undergo condensation with piperidine unless it has been exposed to sunlight or to a quartz lamp. The irradiation is believed to produce a compound, probably $CH_3CH=CHCOOH$, by autoxidation This is thought to be necessary for the condensation.

[153] Farkas, L., and Hirschberg, Y., *J. Am. Chem. Soc*, **59**, 2453 (1937).

[154] Berthelot, D., and Gaudechon, H., *Compt. rend*, **151**, 478 (1910).

[155] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1164 (1910).

[156] Henri, V., and Wurmser, R, *Compt. rend.*, **155**, 503 (1912); see also Porter, C. W., and Iddings, C, *J. Am. Chem. Soc.*, **48**, 40 (1926) and Wiesler, K, *Z angew Chem.*, **40**, 1023 (1927).

[157] Bowen, E. J., and Thompson, H. W, *Nature*, **133**, 571 (1934); Norrish, R. G. W., *Nature*, **133**, 837 (1934); Norrish, R. G. W., Crone, H. G., and Saltmarsh, O. D., *J. Chem. Soc.*, 1456 (**1934**); Scheibe, G., Povenz, F., and Lindström, C. F., *Z. physik. Chem.*, **B20**, 283 (1933). The influence of various substituents has been studied by Lowry, T. M., and Lishmund, R. E., [*J. Chem. Soc.*, 1313 (**1935**)] and by Herold, W., [*Z. physik. Chem.*, **B18**, 265 (1932); *Z. Elektrochem.*, **38**, 633 (1932)]. The effects of solvents of varying polarity have been described by Wolf, K. L., [*Z. physik. Chem.*, **2B**, 39 (1929)], Kremann, R., Pestemer, M., and Bernstein, P., [*Monatsh.*, **61**, 351 (1932)], and Pestemer, M., [*Z. Elektrochem.*, **40**, 493 (1934)].

[158] Ley, H., and Arends, B., *Z. physik. Chem.*, **12B**, 132 (1931); Scheibe, G., and Lindström, C. F., *Z. physik. Chem.*, **B12**, 387 (1931).

[159] Noyes, W. A., Jr., *Rev. Modern Physics*, **5**, 285 (1933). Noyes has recently attempted an interpretation of the near ultraviolet absorption spectrum, *Trans. Faraday Soc*, **33**, 1495 (1937).

[160] Bowen, E. J., and Thompson, H. W., *Nature*, **133**, 571 (1934).

Further evidence came from a study of fluorescence. It was found by Damon and Daniels[161] that acetone vapor shows a green fluorescence when irradiated by wave-lengths shorter than 3130A. It is blue in the presence of a trace of oxygen, but changes to green when the latter has been removed by a photoöxidation of some of the acetone. Norrish, Crone and Saltmarsh,[162] found the absorption spectrum of acetone vapor to consist of a continuous band between about 3000 and 2200A with a few faint maxima, and a region of discrete absorption between 3340A and about 2950A, thus slightly overlapping the continuous region. Fluorescence was produced only by absorption in the continuous region, its maximum intensity being excited by the absorption of the wave-length 3050A. The fluorescence spectrum excited by the mercury arc consisted of three diffuse bands with maxima at 5100, 5600 and 6100A.[163] The specific effect of oxygen was attributed to the removal of oxygen by excited acetone and the formation of a second transient fluorescent substance. The fluorescence of acetone vapor was unaffected by the addition of nitrogen, but its intensity increased with increasing pressure of acetone vapor.[164] The characteristics of the fluorescence were thought to argue against the concept that it arises from excited molecules of the usual type formed in the continuous region. Furthermore, the assumption of Bowen and Thompson that the apparently continuous bands are really composed of unresolved closely packed rotation lines would not account for the abrupt appearance of fluorescence observed to occur at the wave-lengths at which the diffuseness of the bands begins.[164a]

Norrish suggested that the energy absorbed by the chromophoric carbonyl group passes to some other linking or linkings in the molecule by a process similar to the radiationless transfer in a collision of the second kind. A portion may lead to the formation of free radicals by decomposition, a portion may lead to a decomposition of the molecule by a process of the type discussed for aldehydes which produces carbon monoxide and ethane, and a portion, less than 3 per cent, may be lost by fluorescence.

Although Bowen and Watts,[164b] who used nonmonochromatic light, reported a quantum yield of 1.8 for the photolysis of acetone vapor, Damon and Daniels[165] found it much lower, only about one of every five or six absorbed quanta leading to chemical reaction, including both decomposition and condensation processes. The yields were about the same for radiations of 3130 and 2650A. Decreasing the intensity to about one-tenth increased the quantum yield by more than 50 per cent. Reducing the acetone pressure to one-tenth atmospheric reduced the quantum yield to roughly one quarter that at atmospheric pressure.

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[161] Damon, G. H., and Daniels, F., *J. Am. Chem. Soc*, **55**, 2363 (1933).

[162] Norrish, R. G. W., Crone, H. G., and Saltmarsh, O. D., *J. Chem. Soc.*, 1456 (1934).

[163] The visible and diffuse fluorescence is accompanied also by ultraviolet emission of fine sharp lines, interpreted as predissociation in emission by Crone, H. G., and Norrish, R. G. W., *Nature*, **132**, 241 (1933). See also Padmanabhan, R., *Proc. Indian Acad. Sci.*, **5A**, 594 (1937); *Chem. Abs.*, **31**, 8379 (1937). Matheson, M. S., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **60**, 1857 (1938).

[164] But compare, Fisk, C. F., and Noyes, W. A., Jr., *J. Chem. Physics*, **2**, 654 (1934).

[164a] Norrish, R. G. W., *Nature*, **133**, 837 (1934).

[164b] Bowen, E. J., and Watts, H. G., *J. Chem. Soc.*, 1607 (1926).

[165] Damon, G. H., and Daniels, F., *J. Am. Chem. Soc.*, **55**, 2363 (1933).

Condensation reactions occurred only in the presence of traces of moisture. It was suggested that under these conditions diacetone alcohol was produced. The latter could be photolyzed by the wave-length 3650A to the same products of photolysis as those of acetone. The alcohol shows a green fluorescence when irradiated by the wave-lengths 3650, 4050 or 4360A, but only slight fluorescence at 3130A or shorter wave-lengths.

Damon and Daniels found the products of photolysis of acetone to include carbon monoxide, ethane, methane, hydrogen and free carbon. Their mechanism was based on the assumption that activated molecules split off carbon monoxide, the remaining methyl groups combining in more than half the molecules to form ethane. Norrish, Crone and Saltmarsh found 46.6 per cent carbon monoxide, 44.2 per cent ethane and 9.2 per cent of methane and confirmed the quantum yield measurements of Damon and Daniels. Light absorbed both in the regions of discrete and continuous absorption leads to decomposition, the yields being 0.2 at 3150A and 0.4 at 2650A. The full mercury arc gives somewhat less than 10 per cent of methane, possibly derived from a photoreaction in some liquid acetone also present. They believed the primary process to consist, as discussed in connection with their fluorescence observations, in the formation of free methyl radicals and the liberation of carbon monoxide. That the quantum yields were low, even in the continuous region, was accounted for only to a slight extent by the observed fluorescence. They preferred to conceive of the absorbed energy being for the most part degraded to heat by a process of internal stabilization in which the energy absorbed by the carbonyl group is divided up among the various forms of motion possible in the complex molecule. The theory of Norrish is of considerable importance in emphasinzing the possibility that energy absorbed in producing an electronic transition in one part of a molecule need not remain localized if the molecule is complex. The energy absorbed by the carbonyl group amounts to about 90 kcal. It is then partly transferred by resonance to the part of the molecule to be decomposed, about 25-65 kcal. being required for each linking to be broken. The formation of carbon monoxide suggested the simultaneous breaking of two linkages.[166]

Spence and Wild[167] believe that at temperatures below 60°, the primary process may consist in the rupture of but one linking with the formation of methyl and the acetyl radicals, since they were able to isolate large volumes of biacetyl from the liquid products of the photolysis of acetone. They found the ratio of the volume of ethane produced to that of carbon monoxide to be 1.5. At higher temperatures, however, the ratio is unity, and some methane is formed,[168] suggesting that under these conditions, the acetyl radical is short-lived. In the banded absorption region, the decomposition is slow and the ethane to carbon monoxide ratio is nearly one.

The reaction is increased by an increase of temperature, Winkler[169] finding the quantum yield at 100°C. to be five times that at 60°C. This higher yield is maintained up to 400°C. The effect of temperature is much greater when the irradiation is by longer wave-lengths than by shorter ones. This may be due to the fact that the thermal energy of the molecule contributes more to the dissociation process when small quanta are absorbed than when larger ones are employed. At 400°C., the reaction products included a considerable quantity of methane and unsaturated compounds, indicative of the photochemical formation of ketene, $CH_2=C=O$. Leermakers[170] also found the quantum yield for carbon monoxide formation to be nearly unity in the temperature range 200° to 400°C., the carbon monoxide in the reaction products decreasing from 50 per cent to approximately 33 per cent. He also found that methyl radicals do not initiate a chain decomposition of acetone below 400°C.

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[166] Norrish, R. G. W., *Acta Physicochim. U.R.S.S.*, 3, 171 (1935); *Chem. Abs.*, 30, 2493 (1936).

[167] Spence, R., and Wild, W., *Nature*, 138, 206 (1936); *J. Chem. Soc.*, 352 (1937).

[168] See also Taylor, H. S., and Rosenblum, C., [*J. Chem. Phys.*, 6, 119 (1938)], who investigated the reaction in the presence of hydrogen. They believe the major primary process to be dissociation to methyl radicals, and consider especially the activation energies of the secondary processes, concluding the ethane to result either from a wall reaction with zero activation energy or from a bimolecular process of small activation energy.

[169] Winkler, C. A., *Trans. Faraday Soc.*, 31, 761 (1935).

Mention has not yet been made of the fact that the absorption by acetone increases from a minimum at about 2115A toward shorter wave-lengths, photolysis being pronounced below 2000A.[171] A vibrational analysis of the group of bands extending from 1960 to about 1800A has been given by Noyes, Dunning and Manning,[172] who photographed the spectrum down to 1200A and found other bands ascribed to different electron transitions below 1800A. According to Manning,[173] wave-lengths in the range 1900-2000A have little effect on acetone at pressures around 100 mm. The most effective ones are those shorter than 1700A; these produce increased amounts of hydrogen. At very low pressures (0.025 mm.), however, wave-lengths in the range 1850 to 2000A are more effective, but form only small amounts of gaseous hydrocarbons. The presence of a condensed nonvolatile hydrocarbon was suspected. Howe and Noyes[174] find that in this range the quantum yield is independent of the intensity, but increases with decreasing acetone pressure to a limit of 0.65. It is increased by the addition of nitrogen, ethane or carbon dioxide.

In hexane solution, the rate of decomposition is less than when the acetone is in the vapor form, and the quantum yield decreases with increasing acetone concentration.[175] Gases are not evolved and the chief products are a substance capable of absorbing bromine readily, and an alcohol, probably dimethyl-*n*-hexyldimethylcarbinol. Similarly, the reaction in carbon tetrachloride as solvent evolves no gas. In benzene solution, no photochemical reaction occurs.

In an aqueous solution, the production of formaldehyde as well as of acetic acid has been noted by Qureshi and Taher.[176] The quantum yields varied between 0.13 and 0.14 for concentrations 0.05 to 0.5 molar in acetone. The temperature coefficient of the rate was 1.52.[177]

Berthelot and Gaudechon[178] observed that one cc. of a 10-per cent solution of dihydroxyacetone evolved 0.2 cc. of almost pure carbon monoxide during 12 hours of exposure to sunlight. They also studied the behavior of diethylketone.[179]

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[170] Leermakers, J. A., *J. Am. Chem. Soc.*, **56**, 1899 (1934).

[171] Ley, H., and Arends, B., *Z physik. Chem.*, **12B**, 132 (1931).

[172] Noyes, W. A, Jr., Dunning, A. B. F., and Manning, W M, *J Chem. Physics*, **2**, 717 (1934); **3**, 131 (1935); Howe, J. P., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **58**, 1404 (1936).

[173] Manning, W. M., *J. Am. Chem. Soc.*, **56**, 2589 (1934).

[174] Howe, J. P., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **58**, 1404 (1936).

[175] Bowen, E. J., and de la Praudière, E, *J. Chem. Soc.*, 1503 (1934); Bowen, E. J., and Horton, A. T., *J. Chem. Soc.*, 1685 (1936).

[176] Qureshi, M., and Taher, N. A., *Nature*, **127**, 522 (1931); *J Phys. Chem.*, **36**, 2670 (1932).

[177] For the photoöxidation of acetone vapor, see P. Fugassi, *J. Am. Chem Soc.*, **59**, 2092 (1937).

[178] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **155**, 401 (1912).

[179] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **151**, 478 (1910).

Norrish and Appleyard[180] found that, in the light of a mercury arc, about 80 per cent of the molecules of methylethylketone which decompose yield carbon monoxide and a mixture of ethane, propane and butane, the remainder forming ethylene and acetaldehyde.[181] Methylbutylketone yielded propene and acetone. In the range 2480 to 2770A the quantum yield of the decomposition of this ketone at 760 mm. and 127°C. by the process yielding carbon monoxide, methyl and butyl radicals is approximately 0.03, and by that yielding acetone and methylethylene, 0.27. That for condensation or polymerization is approximately 0.04.[182]

The absorption spectrum is diffuse and fluorescence is not observed. Similarly, dipropylketone exhibits two types of change on irradiation.[183] One type (37 per cent of the molecules decomposed) yields carbon monoxide and hexane, and the other (63 per cent) forms ethylene and methylpropylketone. In this reaction, Pearson and Purcell[184] detected the formation of the propyl radical by the mirror test and gave its half-life period as 2.3×10^{-3} second. In cyclohexanone, 10-per cent solutions of methylbutyl ketone and dipropylketone yield 98 per cent of methylethylene and ethylene, respectively, at 20°C. But at 100°C., dipropylketone gave also carbon monoxide and ethane. Two mechanisms accordingly seem necessary. One involves activated molecules with relatively long lives which are readily destroyed by collisions with the solvent molecules. The other involves excited molecules of such short life that the solvent molecules have no time to intervene between the time of activation and the subsequent decomposition.[185]

Saltmarsh and Norrish[186] have decomposed the vapors of cyclopentanone, cyclohexanone and cycloheptanone in the light of a quartz mercury arc. From 80 to 95 per cent of the last-named ketone decomposed to give cyclohexane and carbon monoxide and 4 per cent went to methylethylene. Of the cyclohexanone, 92 per cent gave carbon monoxide and cyclopentane and 8 per cent went to ethylene, methylethylene and carbon monoxide. Half of the cyclopentanone gave ethylene and carbon monoxide and half went to a mixture of propylethylene, *sym*-dimethylethylene and carbon monoxide.

Irradiation of isopropenylmethyl ketone by means of a quartz lamp produces in five days a solid polymer, soluble in acetone and precipitated as a colorless powder by methyl alcohol.[187] Under the same conditions, neither propenylmethylketone nor mesityl oxide polymerizes. The polymerization could take place by 1,4-addition as with rubber, through the carbonyl group analogous to the polyoxymethylenes and by the ethylene linkage with the formation of a paraffin derivative. Combinations of these methods of polymerization would lead to three-dimensional structures, but the solubility of the product did not support the occurrence of such a complication. The molecular weight of the polymer, as determined by the Staudinger viscosity method, was 34000.

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[180] Norrish, R. G. W., and Appleyard, M., *J. Chem. Soc.*, 874 (1934). For results at 100° in liquid paraffin solution, see Norrish, R. G W., and Bamford, C. H., *Nature*, **140**, 195 (1937); Norrish, R. G. W., *Trans. Faraday Soc.*, **33**, 1521 (1937). Here the free radicals react mainly with the solvent rather than combine together.

[181] At 3130A, 11 per cent of the reaction goes to diketones. Biacetyl is also formed when the irradiation is in the range 1850 to 2000A. In this range the quantum yield for carbon monoxide formation increases from 0.7 to 0.88 as the pressure decreases from 90 mm. to 0.1 mm. The total quantum yield for the decomposition approaches unity at low pressures. Ellis, V. K., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **60**, 2031 (1938).

[182] Bloch, B. M., and Norrish, R. G. W., *J. Chem. Soc.*, 1638 (1935).

[183] Bamford, C. H., and Norrish, R. G. W., *J. Chem. Soc.*, 1504 (1935).

[184] Pearson, T. G., and Purcell, R. H., *J. Chem. Soc.*, 253 (1936).

[185] Norrish, R. G. W., and Bamford, C. H., *Nature*, **138**, 1016 (1936).

[186] Saltmarsh, O. D., and Norrish, R. G. W., *J. Chem. Soc*, 455 (1935); see also Norrish, R. G. W., *Acta Physicochim. U.R.S.S.*, **3**, 171 (1935); *Chem. Abs.*, **30**, 2493 (1936).

[187] Staudinger, H., and Ritzenthaler, B., *Ber.*, **67B**, 1773 (1934).

According to Bowen and de la Praudière,[188] liquid benzophenone at 100°C., showed no change after irradiation for nine hours with a mercury arc, and acetophenone no change after seven hours. When a 0.1 molar solution of benzophenone in hexane was irradiated, benzopinacol crystallized out, being formed with a quantum efficiency of 0.04. None was formed when carbon tetrachloride was the solvent.

The quantum efficiency of the photopolymerization of biacetyl in solutions in hexane or ether by wave-lengths between 4360 and 3660A is greater the more dilute the solutions. Bowen and Horton[189] account for this by an explanation which Bowen also used to account for the more rapid decomposition of various ketones in solution than in the pure liquid state. This was to the effect that the primary excited level is not reactive but passes, if not deactivated by a collision within 10^{-12} second, into a second excited level which is reactive.

Ketene. The absorption spectrum of ketene vapor consists of a series of regularly spaced diffuse bands in the region of carbonyl absorption, 3700 to 2600A. The maximum absorption is somewhat displaced to longer wave-lengths occurring at 3100A.[190] No difference exists between the absorption spectra of aldoketenes of the type $H_2C=CO$ and ketoketenes, $R_2C=CO$. There is also a region of continuous absorption beginning at 2200A and ascribed to the ethylene linking. Fluorescence is lacking in ketene.

Irradiation with the mercury arc leads to decomposition with the formation of two volumes of carbon monoxide and one of ethylene. Norrish, Crone and Saltmarsh believe that light energy absorbed by the carbonyl group is transferred to the ethylene group with consequent rupture.

$$CH_2=CO + h\nu \longrightarrow CH_2 + CO$$

This is followed by the process:

$$CH_2 + CH_2=CO \longrightarrow C_2H_4 + CO.$$

Ross and Kistiakowsky[191] interpreted the above-mentioned primary process as due to predissociation in accordance with the nature of the absorption spectrum, no collisions being necessary. They found the decomposition to occur with a quantum yield of approximately unity at 3130A. The accumulation of ethylene stops the reaction. A solid film deposited on the walls of the reaction vessel must have the composition $(CH_2)_n$ since no free carbon deposits were obtained and no hydrogen was liberated.

Ross and Kistiakowsky thought the additional energy required to break the double bond over that available in the absorbed quantum might be derived from the resonance energy of the carbon monoxide formed in the decomposition. The secondary reaction of Norrish was rejected because the quantum yield proved to be unity. The methylene radicals formed in the primary process must react with each other to form ethylene. The slowing down of the reaction by ethylene must be ascribed to the reaction of methylene groups with ethylene with formation of the solid polymer. Thus, methylene radicals appear to combine readily to ethylene in a bimolecular reaction, although methyl radicals do not combine so readily to form ethane. At 3660A, where the banded structure is more pronounced and predissociation less probable, the quantum yield of the reaction, which occurs but slowly at this wave-length, appears to be less than unity.

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[188] Bowen, E. J., and de la Praudière, E., *J. Chem. Soc.*, 1503 (1934).

[189] Bowen, E. J., and Horton, A. T., *J. Chem. Soc.*, 1505 (1934).

[190] Norrish, R. G. W., Crone, H. G., and Saltmarsh, O. D., *J. Chem Soc.*, 1533 (1933); Lardy, G. C., *J. chim. phys.*, **21**, 353 (1924)

[191] Ross, W. F., and Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **56**, 1112 (1934).

Norrish, Crone and Saltmarsh[192] do not agree that the observed quantum yields necessarily exclude the occurrence of their secondary reaction, since it is known that in polyatomic molecules, as acetone, etc., the quantum yield of the primary process may be less than unity throughout a considerable portion of a region of continuous absorption.

Diketones. In α-dicarbonyl compounds, such as glyoxal, the conjugation of the double bonds moves the absorption into the visible.[193] Glyoxal vapor, which has its maximum absorption between 4550 and 4123A, gives as the main products of decomposition carbon monoxide and a solid consisting of a polymer of the hitherto unknown glycerosone, $CH_2OH{\cdot}CO{\cdot}CHO$. About 2 per cent of hydrogen was also obtained as a result of a second reaction.[194]

Schwenk and Borgwardt[195] prepare unsaturated α, β-diketones by subjecting aromatic, hydroaromatic or aliphatic compounds in which a methylene group is directly coupled to an ethylene linkage, to the action of selenium dioxide and ultraviolet rays without heating. Thus, from α-indene is produced a ketone, $C_{10}H_{14}O$.

Biacetyl vapor is decomposed by ultraviolet rays with the production of ethane and carbon monoxide. An aqueous solution yields acetic acid and acetaldehyde.[196] Observations by Grossmann[197] on the absorption spectrum of ethylacetoacetate show that it is decomposed by ultraviolet rays, yielding mainly ethyl acetate and acetic acid. Under the same conditions, acetylacetone gives acetic acid and acetone.[198] Vitoria[199] finds that light from a quartz lamp causes partial polymerization and decomposition of gaseous acetylacetone with formation of carbon monoxide. With light of wave-lengths longer than 3050A, only polymerization occurs. Liquid acetylacetone, or its solution in carbon tetrachloride, undergoes a decided polymerization, but does not decompose to yield carbon monoxide. Walker and Wild[200] find acetyl peroxide to yield on photochemical decomposition, carbon dioxide, methane and some ethane.

Carbohydrates. In contrast to the observations of Bielecki and Henri[201] and of Niederhoff,[202] Henri and Schou[203] found that solutions of very pure dextrose showed no indication of an absorption band due to the carbonyl group at 2800A, most of the molecules having a ring structure. Alkaline solutions, however, exhibit the band, the number of molecules in the aldehydic form depending on the age, temperature and pH of the solution. Similar conclusions have been reported for a number of other sugars, including galactose, levulose, *l*-arabinose, rhamnose, maltose and lactose.[204]

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[192] Norrish, R. G. W., Crone, H. G., and Saltmarsh, O. D., *J. Am. Chem. Soc.*, **56**, 1644 (1934).

[193] Lüthy, A., *Z. physik. Chem.*, **107**, 302 (1923); Purvis, J. E., and McCleland, N. P., *J. Chem. Soc*, **101**, 1810 (1912); Neuberg, C., and Schou, S. A., *Biochem. Z.*, **191**, 466 (1927); Marchlewski, L., Pizlo, J., and Urbanczyk, W., *Biochem Z.*, **264**, 437 (1933).

[194] Norrish, R. G. W., and Griffiths, J. G. A, *J. Chem. Soc.*, 2829 (1928).

[195] Schwenk, E., and Borgwardt, E., German P. 608,136, Jan. 17, 1935, to Schering-Kahlbaum, A.-G.; *Chem. Abs.*, **29**, 6246 (1935).

[196] Porter, C. W., Ramsperger, H. C., and Steel, C., *J. Am. Chem. Soc.*, **45**, 1827 (1923).

[197] Grossmann, P., *Z. physik. Chem.*, **109**, 305 (1924); *Chem. Abs.*, **19**, 39 (1925).

[198] Morton, R. A., and Rosney, W. C., *J. Chem. Soc.*, 706, 713 (1926) and Acly, H. E., and French, H. S., *J. Am. Chem. Soc.*, **49**, 847 (1927) report absorption data on these and related compounds. The enolic and ketonic forms are distinguishable by bands near 2500 and 2700A, respectively

[199] Vitoria, A. P., *IX Congr. intern. quim. pura applicata*, **2**, 334 (1934); *Chem. Abs.*, **29**, 7811 (1935).

[200] Walker, O. J., and Wild, G. L. E., *J. Chem. Soc.*, 1132 (1937).

[201] Bielecki, J., and Henri, V., *Ber.*, **46**, 3627 (1914).

[202] Niederhoff, P., *Z. physiol. Chem.*, **165**, 130 (1927); **167**, 310 (1927); **174**, 300 (1928).

[203] Henri, V., and Schou, S. A., *Z. physiol. Chem.*, **174**, 295 (1928).

The variations in the absorption exhibited by these sugars under various conditions of pH and the effects of impurities may perhaps account for the diverse statements which have been made in regard to their susceptibilities to photolysis. It is generally agreed that aqueous solutions of dextrose, galactose and mannose are not affected by sunlight, although changes[205] may be produced in the presence of such sensitizers as iron or uranium salts.[206] Ghosh and Rakshit[207] claim that visible light increases somewhat the rate of oxygen absorption by glucose or fructose in the presence of cerium hydroxide as catalyst.

Irradiation of 0.1 to 50 per cent glucose solutions with a mercury-vapor arc for fifteen minutes to five hours causes, according to Dillman,[208] no apparent change in optical rotation nor in their ability to reduce alkaline copper tartrate solution. de Fazi[209] believed that sugar solutions which had been irradiated six hours fermented more rapidly than untreated solutions. The induced oxidation of glucose by glutathione is said to be markedly accelerated by light; photosensitizers further accentuate the reaction.[210]

The formation of acid in irradiated dextrose solutions was noted by Euler and Lindberg,[211] who showed that on further action of the ultraviolet rays, there resulted a gaseous mixture containing 15 per cent carbon dioxide, 40 per cent carbon monoxide and 40 per cent hydrogen. Berthelot and Gaudechon,[212] however, found approximately equal volumes of carbon monoxide and methane and about six times as much hydrogen. More recently, Bernoulli and Cantieni[213] noted that at the beginning of the reaction much more hydrogen than carbon monoxide is evolved, but that later the reverse is true. The decomposition was accelerated by acids and retarded by alkalies. No optically active decomposition products were formed, and the decrease in glucose as measured by rotation was not proportional to the amount of carbon monoxide evolved.

Ketoses were found by Berthelot and Gaudechon,[214] to undergo photolysis more readily, and to behave in a manner similar to that of acetone. Levulose, sorbose, perseulose, erythrulose and dihydroxyacetone each gave carbon monoxide, hydrogen and the alcohol with one carbon atom less than the parent sugar. Extreme ultraviolet rays caused secondary reactions, in which carbon dioxide and methane were evolved and the solution became acid. Levulose gave about ten times as much carbon monoxide as of methane.[215] Maltose behaved similarly to dextrose and sucrose gave results intermediate between dextrose and levulose.

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[204] Marchlewski, L., and Kwiencinski, L., *Bull. Acad Polonaise,* 255, 1926A; 379, 1927A; 257, 263, 271, 1928A; 317, 1929A; *Bull. soc. chim.*, **43,** 725 (1928); *Z physiol Chem*, **169,** 300 (1927); Marchlewski, L., and Gabryelski, W., *Bull. Acad. Polonaise,* 397, 1933A; Marchlewski, L., and Urbanczyk, W., *Ibid.*, 409, 1933A; *Biochem. Z.*, **261,** 393 (1933); Fischler, F., Hauss, H, and Taufel, K, *Biochem. Z.*, **265,** 181 (1933); Braun, E., *Ber.*, **63B,** 1972 (1930); Kwiencinski, L., Mayer, J., and Marchlewski, L., *Z. physik. Chem.*, **176,** 292 (1928); Bednarczyk, W, and Marchlewski, L, *Bull. Acad Polonaise,* 140, 1937A; *Chem. Abs.*, **32,** 1576 (1938); Goos, F., Schlubach, H., and Schroter, G., *Z. physik. Chem.*, **186,** 148 (1930). For absorption data on glucosides, see Marchlewski, L, and Mayer, J., *Bull. Acad. Polonaise,* 111 (1929); Ramart-Lucas, Mme., and Rabate, J., *Compt rend.*, **196,** 1493 (1933). For hexose phosphates, Neuberg, C., and Schou, S. A., Biochem. Z, **191,** 466 (1927).

[205] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **155,** 831 (1912)

[206] Neuberg, C., *Biochem. Z.*, **39,** 158 (1912); Abelous, Aloy and Valdiguè, *Compt. rend. soc. biol.*, **96,** 1385 (1927).

[207] Ghosh, J. C., and Rakshit, P. C., *J. Indian Chem. Soc.*, **12,** 357 (1935); *Brit. Chem. Abs.*, **1935A,** 1329.

[208] Dillman, L. M, *J. Lab. Clin. Med.*, **17,** 236 (1931); *Chem. Abs.*, **26,** 3270 (1932).

[209] de Fazi, R., *Atti accad. Lincei,* **5,** 344, 901 (1927); *Chem. Abs.*, **21,** 4013 (1927); Sanzo, L., and Pirrone, F., *Atti accad. Lincei,* **13,** 613 (1931); *Chem. Abs.*, **26,** 2990 (1932).

[210] Palit, C. C., and Dhar, N. R, *J. Indian Chem. Soc.*, **11,** 661 (1934); *Brit. Chem. Abs.* **1934A,** 1314. See also *J. Phys. Chem.*, **32,** 1263 (1928).

[211] Euler, H., and Lindberg, E., *Biochem. Z.*, **39,** 410 (1912); *J. Chem Soc.*, **102,** II, 407 (1912).

[212] Berthelot, D., and Gaudechon, H., *Compt rend.*, **151,** 395 (1910).

[213] Bernoulli, A. L., and Cantieni, R., *Helv. Chim. Acta,* **15,** 119 (1932).

[214] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **155,** 401, 1153 (1912); *Bull. soc. chim.*, **35,** 241 (1924); see also Beyersdorfer and Hess, *Ber.*, **57B,** 1708 (1924).

The decomposition of the latter sugar gave also formaldehyde and methanol.[216] It was believed that this sugar was very slowly decomposed by sunlight, 0.54 cc. of almost pure carbon monoxide being produced in two months.[217]

The use of this behavior of a 10 per cent fructose solution in ultraviolet actinometry, proposed by Berthelot and Gaudechon,[218] has been more recently studied by Bernoulli and Cantieni.[219] In dilute solutions (4.5 to 18 g. per liter), the velocity is proportional to the concentration but in strong ones (720 to 1080 g. per liter), it is constant. The proportion of carbon dioxide in the gases evolved varies inversely with the light intensity. Acids appear to be formed only in solutions heated to 80°C. The evolution of gases is accelerated by sodium chloride and retarded by potassium bromide and iodide and acids or bases. The photolysis also occurs in methanol or glycerol solutions and in these is more accelerated by small amounts of water than by larger ones. The reaction can be produced by radiations passing through glass, but is much slower than in quartz, since only those fructose molecules possessing the ketonic structure evolve carbon monoxide. Molecules with ring structures are believed to yield carbon dioxide. At ordinary temperatures, the reaction, once started, may continue for hours after stopping the irradiation, but at high temperatures, the after-effect is very slight. The course is believed to involve the intermediary formation of a peroxide, perfructose. A yellow color (photopyridine) developed by light in solutions of pyridine, water and fructose is more readily formed and more readily bleached than it is in solutions in which the fructose is replaced by glucose, galactose, sucrose or lactose. Acetone inhibits its formation. Methanol is almost without influence on the color reaction, but has a greater retarding influence on fading than has fructose. Pure ethanol retards color formation, but the color once formed is more stable in ethanol than in methanol.

Holtz [220] finds the ultraviolet irradiation of aqueous sugar solutions (glucose, fructose, arabinose) and sugar-like solutions (glycerol, sorbitol, glucosamine) to produce substances which form systems with strong negative redox potentials. The products are believed to accelerate the autoxidation of cysteine and adrenaline. Dubouloz [221] added eosin (1 : 5000) to a 0.05 molar solution of glucose in a phosphate buffer solution of pH 7.7, and freed the solution of dissolved oxygen. After sufficient illumination by a tungsten lamp, the oxidation-reduction potential descended to −210 mv., the equilibrium point of oxygen-free glucose solutions. Further illumination caused a further descent. If this did not exceed 350 mv., the phenomenon was reversible, and upon standing in the dark, the value −210 mv. was regained.

The oxidation of glucose by hydrogen peroxide in acid medium photosensitized by tungstic acid appears to follow the unimolecular rate law when the peroxide concentration is low and to be of zero order when it is high.[222] There is an induction period, which increases with the peroxide concentration. The velocity varies as the square root of the intensity of absorbed light, but is independent of the glucose concentration. The quantum yield is somewhat greater than unity and the temperature coefficient, 1.1 to 1.2. Similar reactions occur with formaldehyde and fructose.

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[215] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **151**, 395 (1910).

[216] Bierry, H., Henri, V., and Ranc, A., *Compt. rend.*, **151**, 316 (1910); *Biochem. Z.*, **64**, 257 (1914); *Bull. soc. chim*, **35**, 771 (1924).

[217] Berthelot, D., and Gaudechon, H., *Compt rend.*, **155**, 401 (1912).

[218] Berthelot, D., and Gaudechon, H., *Compt rend.*, **156**, 707 (1913).

[219] Bernoulli, A. L., and Cantieni, R., *Helv. Chim. Acta*, **15**, 119 (1932); Cantieni, R, *Ibid.*, **17**, 1528 (1934); **18**, 473, 933, 1420 (1935); **19**, 86, 94, 270, 276 (1936); *Ber.*, **69B**, 2286 (1936).

[220] Holtz, P., *Arch. exptl. Path. Pharmakol*, **182**, 141 (1936); *Brit. Chem. Abs.*, **1936A**, 1094.

[221] Dubouloz, P., *Compt. rend. soc. biol.*, **116**, 435 (1934); *Chem. Abs.*, **28**, 6371 (1934).

[222] Banerjee, T., *J. Indian Chem. Soc.*, **14**, 59 (1937); *Chem. Abs.*, **31**, 5275 (1937). See also Ghosh, J. C., and Mukherjee, J., *Ibid.*, **6**, 231 (1929).

Neutral solutions of sucrose are hydrolyzed by ultraviolet light and become slightly acid.[223] The rate of hydrolysis increased with the duration of the exposure, probably because of the acid formation, although this may have been due to traces of a catalyst. According to Bierry, Henri and Ranc,[224] the ultraviolet hydrolysis is appreciable in 5 per cent sucrose solutions after twenty hours of irradiation at 40°C.; after 48 hours formaldehyde can be detected. A gas evolution begins after 72 hours and becomes marked on the fifth or sixth day of exposure. Of the combustible part of this gas, 50 per cent was carbon monoxide.

Berthelot and Gaudechon,[225] confirmed the presence of two stages in the hydrolysis of disaccharides by relatively long wave-lengths. The first stage does not evolve gas, but the second consists in the decomposition of the mixture of monoses produced in the first stage and so is accompanied by the evolution of gas. They disagreed with previous observers, in that they did not find that acid is formed during the process. Beyersdorfer and Hess [226] using carefully purified sucrose and conductivity water found that at 15-20°C. in $\frac{1}{8}$ molar solution, the effect of irradiation was hardly perceptible. At 70° and 100°C., the sugar was attacked energetically, the decomposition at first increasing slowly, then rapidly, with increasing temperature. After the addition of 0.3 to 0.6 gram of chlorophyll to 250 cc. of $\frac{1}{8}$ molar solution, irradiation for twelve hours at 100°C. produced no detectable change in the sucrose. Manganese chloride, potassium chloride, potassium bromide, and potassium iodide had little influence on the change, which, however, scarcely occurs in the presence of sodium acetate.

In 0.5 molar solution at 100°C., gas evolution begins in 15 minutes, and the acidity and reducing power increase about in proportion to the time. After about four hours, the solution becomes levorotatory and after 24 hours contains no further positively detectable amounts of optically active substances. The reducing power reaches its maximum after about 48 hours, then decreases proportionately with the time and more slowly than it had increased. A crystal of sucrose when exposed to ultraviolet rays at 70°C. becomes coated on the exposed surface with a brown layer of caramel.

Yajnik, Goyle and Wadhera [227] maintain that aqueous sucrose solutions contained in Jena glass vessels undergo inversion when exposed to tropical sunlight in the absence of acid, and that in the presence of 0.25 normal acid, the rate of inversion is increased by sunlight. Some have believed visible and near infrared rays to effect the inversion with a high quantum yield, the reaction having also a high temperature coefficient.[228] Tanret [229] finds sucrose to be hydrolyzed slowly and maltose and trehalose to be hydrolyzed less than 30 per cent as fast as sucrose by ultraviolet rays. The effect on lactose was uncertain. Szalay[230] suggested that pure sucrose solutions were not affected, but that those containing traces of glucose as catalyst, showed increased reducing power and acidity, ascribed by him to the formation of glucuronic acid.

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[223] v. Euler, H., and Ohlsen, H., *J. chim. phys.*, **9**, 416 (1911).

[224] Bierry, H., Henri, V., and Ranc, A., *Compt. rend.*, **152**, 1629 (1911).

[225] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **155**, 1016 (1912); **156**, 468 (1913).

[226] Beyersdorfer, P., and Hess, W., *Ber.*, **57B**, 1708 (1924); Taketomi, N., and Miura, K., *J. Soc Chem. Ind. Japan*, **33**, 9B (1930).

[227] Yajnik, N. A., Goyle, D. N., and Wadhera, M. L., *Z anorg. Chem.*, **225**, 24 (1935).

[228] Bhattacharya, A. K., and Dhar, N. R., *J. Indian Chem. Soc*, **6**, 879 (1929); *Brit. Chem Abs*, **A**, 555 (1930); *Z. anorg. Allgem. Chem.*, **199**, 1 (1931); see also Andant, A., and Rousseau, E., *Compt rend.*, **186**, 365 (1928).

[229] Tanret, G., *Compt. rend.*, **202**, 881 (1936); *Bull. soc. chim. biol.*, **18**, 1344 (1936).

[230] Szalay, S., *Magyar Biol. Kutato Intezet Munkai*, **8**, 417 (1935-6); *Chem. Abs.*, **30**, 7041 (1936).

Souty[231] directed two pencils of light from the same source, differing only in the direction of their circular polarization, on two identical solutions of a sugar which exhibits mutarotation. Differences in the rate of mutarotation, giving temporary differences which reached more than 0.25° were observed, but the same final equilibrium was obtained. In monochromatic light, glucose gave a positive result at 5461A and a negative one at 5890-6A.

In the case of the trioses, raffinose, melesitose and gentianose, the first stage of the reaction did not appear to consist of the formation of a monose and a biose.[232] After the first stage of decomposition, the action was the same as in the case of the monoses.

When a concentrated aqueous solution of trihexosan is exposed to ultraviolet rays for 56 hours, 60 per cent conversion into hexahexosan occurs; further irradiation of the latter appears to have no action.[233] Irradiation of dextrinosan, $C_{12}H_{20}O_{10}$, affords hexahexosan.

Massol[234] stated that if solutions of soluble starch (prepared by heating for three hours at 150°C.) of 0.2 to 1 per cent concentration, are exposed at a distance of 10 centimeters, to the action of a mercury-vapor quartz lamp consuming 300 watts, the starch gradually loses the property of giving a blue color with iodine, the color undergoing an alteration similar to that observed when the iodine test is applied at various stages of starch conversion. The rate of transformation increases on decreasing the concentration and on acidifying the medium. As a result of the exposure also, the solution acquires reducing power (probably due to maltose) and becomes less precipitable by alcohol. The portion soluble in alcohol possesses reducing power and is dextrorotatory. The hydrolysis was not due to the acidity or temperature or to the small amount of hydrogen peroxide formed under the action of the rays. According to Bielecki and Wurmser,[235] the hydrolysis is accompanied by a partial oxidation, since there can be identified among the products, besides dextrins, reducing sugars, including pentoses, some formaldehyde and other similar substances.

Samec[236] found that on exposing thin layers of potato starch in presence of air to the rays of a quartz lamp, it became yellow and the odor of acraldehyde was observed. The properties of solutions obtained by heating starch so treated under pressure with water indicate that considerable peptization had occurred, together with a certain amount of oxidation and hydrolysis. The behavior on electrodialysis depends on the length of exposure to the ultraviolet, the amount of "gel" being smaller the longer the exposure. The phosphorus of the starch remains largely in organic combination. The cleavage products separated by ultrafiltration, although possessing a lower optical rotation, show the typical iodine colorations of the amylo-compound. Observations have also been made at 50°C. on starch which has been previously dried, or washed with hydrochloric acid and dried and exposed to ultraviolet light in a stream of dry nitrogen and in closed vessels in an atmosphere of nitrogen, whereby oxidation and hydrolysis are prevented. The solutions prepared under pressure from the exposed starch are sometimes cloudy and deposit a precipitate on centrifuging. Wheat starch is also peptized by ultraviolet light, and in this case the behavior of the solution on electrodialysis is the reverse of that of the unexposed starch. As with potato starch, a relatively simple organic acid containing phosphorus is found in the anode cell on electrodialysis.

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[231] Souty, P., *Compt. rend.*, **199**, 198 (1934).

[232] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **155**, 1506 (1912).

[233] Pictet, A., and Vogel, H., *Rec. trav. chim.*, **48**, 843 (1929); *Brit. Chem. Abs.*, **1929A**, 1167.

[234] Massol, L., *Compt. rend.*, **152**, 902 (1911).

[235] Bielecki, J., and Wurmser, R., *Compt. rend.*, **154**, 1429 (1912).

[236] Samec, M., *Kolloid. Chem. Beih.*, **23**, 377 (1927); *Brit. Chem. Abs.*, **A**, 412 (1927).

The changes which take place when starch, glycogen, inulin, dextrin, amylose and amylopectin are irradiated with the quartz mercury lamp have been followed quantitatively by Lieben, Löwe and Bauminger[237] in respect to lactic acid and reducing substance produced. The latter consists not merely of glucose but also of maltose and other reducing sugars, including traces of triose. Amylose and amylopectin are less affected than is starch.[238]

It is claimed by Tanret and Guillaume[239] that 2-per cent solutions of glucosides (salicin, amygdalin, etc.) and also certain esters may be hydrolyzed by exposures to wave-lengths in the range 1800 to 3100A for three to twenty-four hour periods. An increase in temperature or acidity of the medium increases the rate. In the case of nine glucosides, the order of hydrolysis differed when the hydrolyzing agent was ultraviolet rays, acids, and enzymes.[240] After twelve hours of irradiation, various glucosides were hydrolyzed to the following percents: helicin, 100 per cent, gentiopicrin, 59, coniferin, 55.4, amygdalin, 35.4, salicin, 31.1, picein, 23.3, arbutin, 13.4 and methylarbutin, 8.1 per cent. Floridoside (glyceryl α-galactoside) and α- and β-methylglucosides were hydrolyzed very slowly and xanthorhamnin not at all, although it absorbed the entire ultraviolet spectrum used. Acetylsalicylic acid, tropacocaine, homotropococaine, monobutyrin and asparagine were hydrolyzed more or less, but ethyl acetate, glycylglycine, *dl*-alanylglycine, glycyltyrosine, and urea were not.[241] Saponin is claimed by Wolf[242] to lose its toxicity after irradiation by ultraviolet in solution, so that it may be used as an emulsifying agent in food products without danger of producing hemolysis.

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[237] Lieben, F., Löwe, L., and Bauminger, B., *Biochem. Z*, **271**, 209 (1934).

[238] See also Isemura, T., *J. Chem. Soc. Japan*, **56**, 772 (1935); *Chem. Abs.*, **29**, 7352 (1935).

[239] Tanret, G., and Guillaume, A, *Compt. rend*, **201**, 1057 (1935).

[240] Tanret, G., *Compt. rend.*, **202**, 881 (1936); *Bull. soc. chim. biol.*, **18**, 1344 (1936); *Brit. Chem Abs*, **1936A**, 572.

[241] Guillaume, A., and Tanret, G., *Compt. rend.*, **201**, 1057 (1935); *Bull. soc. chim. biol.*, **18**, 556 (1936); *Chem. Abs.*, **30**, 5503 (1936).

[242] Wolf, J., German Patent 524,892, June 3, 1927; *Chem. Abs.*, **25**, 4326 (1931).

Chapter 24

Acids and Other Aliphatic Compounds

The action of ultraviolet light on many organic acids or their salts leads to decomposition [1] of the latter, but in unsaturated acids the polymerizations and stereoisomeric transformations characteristic of the photochemical behavior of double bonds often occur.

Ley and Arends [2] showed that saturated mono- and di-carboxylic aliphatic acids, in vapor form, in hexane, or in aqueous solutions have an absorption band beginning at about 2400A, with a maximum at 2040-2070A. This maximum is ascribed to the carbonyl group, since it appears also in the chlorides and anhydrides of the acids. The nature of the absorption is not materially affected by ester formation, but is usually totally changed by salt formation. Sodium acetate, considered as typical of the salts of acetic acid, shows no maximum at 2040A, but continues to absorb the shorter wave-lengths with increasing intensity. The curve for formic acid lies somewhat nearer to the visible. Ramsperger and Porter [3] found the bimolecular form of formic acid primarily responsible for the absorption between 2260 and 2500A. Harris [4] believed the unimolecular form to agree in absorption with that of the other acids, having its maximum at 2050A.

Lederer [5] finds some specific absorption by all fatty acids between 2700 and 2800A, that of propionic extending to 2700A and stearic to 2800A. A confirmation has been given by Hartleb,[6] but the cause of this absorption has not yet been definitely established.

There is spectroscopic evidence for the formation of solvates of both esters and free acids in various solvents [7] and Herold [8] concludes from ultraviolet absorption measurements that the formation of solvates (hydrates or semiacetals) is a necessary preliminary to the dissociation of the fatty acids.

ACETIC ACID

In the photolysis of acetic acid in the absence of air, Berthelot and Gaudechon [9] obtained a gas which contained 44 per cent of carbon dioxide, 17 per cent of carbon monoxide and 39 per cent of combustible gases. Farkas and Wansbrough-Jones [10] find that undissociated formic, acetic and succinic acids in aqueous solution undergo several simultaneous photochemical changes. One is the direct formation of carbon dioxide and a hydrocarbon by a process analogous to that encountered in the photochemistry of the ketones, $RCOOH + h\nu \rightarrow CO_2 + RH$. With acetic and propionic acids, the reaction, $RCOOH(H_2O) + h\nu \rightarrow CO + H_2O + ROH$ occurs (in aqueous solution) about 60 per cent as frequently as the reaction yielding carbon dioxide. Longer-chained acids tend, as do the aldehydes, to yield some unsaturated hydrocarbon and a shorter-chained acid: $CH_3CH_2CH_2COOH + h\nu \rightarrow C_2H_4 + CH_3COOH$. All of the acids yield condensation products.

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[1] Kailan, A., *Monatsh*, **34**, 1209 (1913).

[2] Ley, H., and Arends, B., *Z. physik. Chem.*, **B4**, 234 (1929); **B17**, 177 (1932); Price, W. C., and Evans, W. M., *Proc. Roy Soc.*, **A162**, 110 (1937); earlier observations are due to Hantzsch, A., and von Halban, H., *Z. Elektrochem.*, **29**, 221 (1923).

[3] Ramsperger, H. C., and Porter, C. W., *J. Am. Chem. Soc.*, **48**, 1267 (1926).

[4] Harris, L., *Nature*, **118**, 482 (1926).

[5] Lederer, E. L., *Allgem. Öl.-u. Fettztg.*, **27**, 237 (1930), *Chem. Abs.*, **25**, 2014 (1931).

[6] Hartleb, O., *Strahlentherapie*, **39**, 442 (1931).

[7] Ley, H., and Hunecke, H., *Ber.*, **59**, 510 (1926).

[8] Herold, W., *Z. physik. Chem.*, **B18**, 265 (1932); *Z. Elektrochem.*, **38**, 633 (1932)

[9] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **156**, 68 (1913); *J. Soc. Chem. Ind.*, **29**, 1081 (1911).

[10] **Farkas, L., and Wansbrough-Jones, O. H.,** *Z. physik. Chem.*, **B18**, 124 (1932).

In acetic acid vapor, which shows only a continuous spectrum, the chief reaction is dissociation into carbon dioxide and methane. The quantum yield (1850-2300A) is 0.45 for acetic acid, 1.0 for propionic acid and 0.4 for succinic acid. When polymers of the acids are present, the reaction is more complex. (See formic acid.) When acetic acid is decomposed in hexane solution, the solvent is attacked.

Burton,[11] using the mirror method, has found that hydrogen atoms but not methyl radicals are formed in the photolysis of acetic acid. Terenin[12] has also detected the hydroxyl radical in photolyses at about 1560A. To account for these results, Burton suggested two possible mechanisms, one being:

$$\begin{aligned}
&CH_3COOH + h\nu \longrightarrow CH_3COOH^*\\
&CH_3COOH^* \longrightarrow CH_3COO + H\\
&CH_3COO + H \longrightarrow CH_4 + CO_2\\
&CH_3COOH + H \longrightarrow CH_4 + COOH\\
&COOH \longrightarrow CO + OH\\
&CH_3COOH + OH \longrightarrow CH_3COO + H_2O\\
&2CH_3COO \longrightarrow C_2H_6 + 2CO_2.
\end{aligned}$$

In aqueous solutions of salts of aliphatic acids the decomposition is even more complex and, according to Jaeger and Berger,[13] is dependent upon the acid anion and other ions which may be present, particularly cations. According to Farkas and Wansbrough-Jones, the reaction depends upon absorption within the electron affinity spectrum of the anion by the process: $A'(H_2O) + h\nu \rightarrow A + OH' + H$, but because of a subsequent reaction $A + H \rightarrow A' + H^+$, the yield of the decomposition products is small. Addition of alkali favors the evolution of hydrogen and the formation of acids of higher basicity. Farkas states[14] the quantum yield of the reaction of the primarily produced hydrogen atom with acetate ion to form methane and carbon dioxide is 0.05 at pH 8.5. When silver acetate is used the hydrogen atoms may react with silver ions, so that the usual retarding process is less effective.

Acetic acid and aniline[15] in equimolar proportions when exposed to ultraviolet rays for 24 hours give nearly a 100 per cent yield of acetanilide. Propionic and benzoic acids act similarly. The yield of propionanilide is about 65 per cent of theoretical and that of benzanilide considerably less. Amide formation occurs much less readily, ammonium acetate in the presence of excess ammonium hydroxide giving only about 5.3 per cent acetamide, and ammonium benzoate even less benzamide.

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[11] Burton, M., *J. Am. Chem. Soc.*, **58**, 692, 1645 (1936). Data for the photolysis of propionic acid have been given by Henkin, H., and Burton, M., *Ibid.*, **60**, 831 (1938). As in acetic acid, both hydrogen atoms and ultimate molecules are produced in primary processes. The relative number of hydrogen atoms per einstein is greater than in acetic acid.

[12] Terenin, A., *Acta Physicochim. U.R.S.S.*, **3**, 181 (1935).

[13] Jaeger, F. M., and Berger, G., *J. Chem. Soc.*, **119**, 2070 (1921); *Proc. Roy Soc.*, **23**, **84** (1920).

[14] Farkas, L., *Z. physik. Chem.*, **B23**, 89 (1933).

[15] Stoermer, R., and Robert, E., *Ber.*, **55B**, 1030 (1922).

dl-α-Iodopropionic acid soon becomes colored by free iodine in daylight, and loses its iodine more rapidly in direct sunlight, or in chloroform solution in glass.[16]

FORMIC ACID[17]

Ramsperger and Porter[18] accomplished the complete decomposition of formic acid vapor by exposing the acid for 16 hours at a distance of 20 cm. from a 220-volt mercury arc at 20°C. Carbon monoxide and water constituted 64 per cent, and carbon dioxide and hydrogen, 36 per cent, of the mixed products formed by two photolytic processes. Müller and Hentschel[19] believed that some of the hydrogen formed reduces the acid further. Although the formation of methanol and formaldehyde could not be established, a noncrystalline solid was observed to form in the solution. They found also that the decomposition could be catalyzed by finely dispersed platinum.

Double molecules of formic acid present in the vapor phase decompose almost entirely to carbon dioxide and hydrogen.[20] The single molecules yield both these products and carbon monoxide and water, the ratio varying with the temperature and wave-length employed. At 40°C. and 2540A, the ratio is approximately 75.5 per cent carbon monoxide and water to 24.5 per cent carbon dioxide and hydrogen. At 100°C. and with the same wave-length, the amounts are 69 and 31 per cent, respectively. At shorter wave-lengths, 2100 and 1900A, the ratio is 42 per cent to 58 per cent. At these two latter wave-lengths, the quantum yield is unity for the decomposition of either double or single molecules.

An application of the para-hydrogen conversion test for atomic hydrogen showed only minimal formation of hydrogen atoms and carboxyl radicals, so that the primary process may consist in a rearrangement of bonds to give hydrogen and carbon dioxide directly. Burton[21] was unable to detect hydrogen atoms by the mirror test. Terenin,[22] however, detected OH by its emission spectrum when wave-lengths near 1560A were used.

According to Allmand and Reeve,[23] radiation of wave-length 3100A produces a slow decomposition of aqueous solutions of formic acid, the products being carbon dioxide and hydrogen, traces of formaldehyde and some more complex compound of highly reduced nature. The latter products were secured by reduction of formic acid by some of the hydrogen. In the presence of the uranyl ion, the decomposition in aqueous solutions is sensitized to visible light.[24] The velocity of photolysis depends upon the concentrations of the formic acid and the uranyl ion. With increasing concentrations of the latter, the velocity at first increases rapidly and passes through a maximum. The reaction is strongly desensitized by iodide, chloride and ferrous ions, hydroquinone, potassium dichromate, silver nitrate, sodium nitrite, potassium cyanide and mercuric sulfate, slightly desensitized by cupric sulfate, chromic sulfate, sodium nitrate and potassium fluoride. Photolysis is not affected by trisodium phosphate, ammonium acetate or magnesium sulfate. Oxidation-reduction properties of the desensitizer, which remains unchanged, play an important part in its effect. Increased concentration of the formic acid diminishes the effect of a desensitizer, but at 25 per cent concentration the velocity becomes almost independent of the concentration. When the concentration of the desensitizer is increased, the desensitizing effect increases rapidly at the beginning and then more slowly. Ghosh and Mitter[25] have given spectroscopic evidence for the formation of intermediate compounds of uranyl salts and organic acids.

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[16] Hannerz, E., *Ber.*, **59B**, 1367 (1926).

[17] It has been claimed that methyl alcohol vapor and carbon monoxide exposed to ultraviolet rays or led over barium and potassium carbonates at 500°, give methyl formate and high-molecular compounds. Wietzel, G., and Wietzel, R., German P. 442,125, June 10, 1923, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **1928B**, 8.

[18] Ramsperger, H. C., and Porter, C. W., *J. Am. Chem. Soc.*, **48**, 1267 (1926).

[19] Müller, E., and Hentschel, H., *Ber.*, **59**, 1854 (1926).

[20] Gorin, E., and Taylor, H. S., *J. Am. Chem. Soc.*, **56**, 2042 (1934); see also Herr, W. N., and Noyes, W. A., Jr., *Ibid.*, **50**, 2345 (1928).

[21] Burton, M., *J. Am. Chem. Soc.*, **58**, 1655 (1936).

[22] Terenin, A , *Acta Physicochim. U.R S.S.*, **3**, 181 (1935).

[23] Allmand, A. J., and Reeve, L., *J. Chem. Soc.*, 2852 (**1926**).

[24] Ouellet, C., *Helv. Chim. Acta*, **14**, 936 (1931); *Chem. Abs.*, **26**, 656 (1932), Büchi, P. F., [*Z. physik. Chem*, **111**, 269 (1924)] gives the quantum yield as 0.7.

A reaction in aqueous solution between sodium formate and iodine studied by Dhar and Bhargava[26] is unimolecular in darkness and "semimolecular" in light. Its velocity is proportional to the 0.75 to 0.66 power of the intensity of the incident light. It is a chain reaction, the quantum yield varying from 26 to 64, increasing with temperature and frequency of the light. More light is absorbed by the mixture than by the reactants separately.

Attention has been called to the formation of a peroxide from formic acid in the presence of oxygen, by short ultraviolet rays. The peroxide was assumed by Cantieni[27] to be performic acid.[28]

Relatively little work has been done on the photolysis of acetyl halides. The decomposition products contain carbon monoxide and the methyl halide, but no hydrogen, ethane or ethylene. The decomposition products from acetyl chloride contained hydrogen chloride and a polymer of either biacetyl or ketene. The products from acetyl bromide are bromine and CH_2BrCH_2Br(?). Iodine is formed from acetyl iodide.[29]

The rates of decomposition of carbonyl hypohalites, *e.g.*, C_2H_5COOBr, are dependent both upon concentration and illumination, according to Bockemüller and Hoffmann,[30] daylight greatly retarding the decomposition.

DIBASIC ACIDS

The photolysis of oxalic acid[31] consists in a primary decomposition into carbon dioxide and formic acid, followed by a secondary decomposition of the formic acid into carbon monoxide and hydrogen by rays of short wave-length. Kailan[32] concluded that the rate of the decomposition of dibasic acids increases with the duration of the exposure, but does not increase in proportion to the concentration of the acid. He found more carboxyl groups to be decomposed from malonic acid than from oxalic acid. Also, introduction of a hydroxyl group increased the rate of decomposition of dibasic acids. The rate of decomposition of malonic acid by sunlight in the presence of catalyst was found by Fay[33] to be exceedingly slow. Berthelot and Gaudechon[34] found uranyl salts to catalyze this reaction, and Volmar[35] found the main products of decomposition to be acetic acid and carbon dioxide.

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[25] Ghosh, J. C., and Mitter, B. N., *Quart. J Indian Chem. Soc.*, **4,** 353 (1927); *Chem. Abs.*, **22,** 1899 (1928).

[26] Dhar, N. R., and Bhargava, P. N., *J. Phys. Chem*, **39,** 1231 (1935).

[27] Cantieni, R., *Helv. Chim. Acta*, **19,** 1153 (1936); *Ber*, **69B,** 1153 (1936) Similar behavior is shown by other fatty acids. *Z. wiss. Phot*, **36,** 90 (1937); *Chem. Abs*, **31,** 8381 (1937).

[28] Data on the decomposition of acetyl peroxide have been given by Walker, O. J., and Wild, G. L. E., *J. Chem. Soc.*, 1132 (**1937**).

[29] Etzler, D. H., and Rollefson, G. K., *J Chem. Phys*, **6,** 653 (1938).

[30] Bockemuller, W., and Hoffmann, F. W., *Ann.*, **520,** 165 (1935); *Chem. Abs.*, **29,** 7940 (1935).

[31] Berthelot, D., and Gaudechon, H., *Compt rend*, **158,** 1791 (1914).

[32] Kailan, A, *Monatsh.*, **34,** 1209 (1913).

[33] Fay, H., *Am Chem. J.*, **18,** 269 (1896).

[34] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **157,** 333 (1913).

Volmar also subjected a series of dibasic acids in 0.01 molar solutions to the light of a quartz mercury arc. Oxalic and malonic acids yields formic and acetic acids, respectively. Succinic acid gave a trace of propionic acid, but glutaric acid gave no butyric acid and liberated only 0.13 cc. of carbon dioxide in four hours. Oxalic acid, like formic acid, has the maximum sensitivity of the corresponding series of acids and has an absorption maximum at 2500A.[36] As the chain between the carboxyl groups lengthens, their mutual influence diminishes and from succinic acid onwards the groups behave as though they were independent.

Noyes and Kouperman[37] found a long induction period for the photolysis of solid oxalic acid by wave-lengths shorter than 2500A. Following the induction period, the rate of decomposition attained a practically constant rate. This rate was apparently greater when short wave-lengths were employed. Their explanation was that such radiations might endow the decomposition products with an excess of kinetic energy which would aid their more rapid diffusion out from the interior of the crystals. The rate of thermal decomposition of solid silver oxalate may be increased by a previous exposure of the salt to light of wave-lengths less than 5200A.[38]

It was reported by Noyes and Kouperman that the rate of decomposition of oxalic acid was greater when the acid was in aqueous solution than when the acid was used alone. Allmand and Reeve[39] found the decomposition products of such solutions to be predominantly carbon dioxide, with small amounts of formaldehyde.[40] Wave-lengths as long as 3000A were effective in causing photolysis. In all cases, the quantum yields were low, but appeared to increase on dilution of the solution. For a 0.68 molar solution, 100 quanta were absorbed per molecule decomposed at 2650A, 2450 at 3000A and 1060 at 3650A.

Winther and Oxholt-Howe[41] found the quantum sensitivity of the decomposition of iron oxalate, succinate, tartrate, citrate and acetate for short wave-lengths to be greater than unity. Kunz-Krause and Manicke[42] reported that under the catalytic action of ferric chloride, 5.3 per cent of crystalline oxalic acid suffers decomposition after a five-hour arc light exposure and 61.7 per cent after 16 hours. Padoa and Vita[43] studied the action of light on the reaction

$$2FeCl_3 + H_2C_2O_4 \longrightarrow 2FeCl_2 + 2HCl + 2CO_2.$$

They believed that the sum of the effects obtained in the blue and violet regions is 1.123 times that of white light. In the presence of quinine bisulfate, the zone of active radiations was widened and the sum of the effects of blue, green and violet lights was said to be 2.125 times that of white light.

Complex Oxalate Ions. The quantities of potassium cobaltioxalate[44] decomposed by the mercury arc in quartz vessels in identical intervals of time were approximately independent of the initial concentrations and determined chiefly by the light energy absorbed. The addition of alcohol had no appreciable effect, but neutral salts did have marked effects. Bhagwat and Dhar,[45] found the reaction to be greatly accelerated by short wave-length radiation. Also, the latter investigators gave the temperature coefficient of the thermal reaction as 3.7. In incandescent light, the coefficient was 1.85 and in sunlight 1.13. In sunlight the velocity was proportional to the square root of the light intensity, but in lamp light it was directly proportional to the intensity. Murgulescu [46] also finds the decomposition of 0.02-0.002 molar potassium cobaltioxalate by light of wave-lengths 4360, 4050, 3660 and 3130A to be of zero order.

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[35] Volmar, *Compt. rend.*, **180**, 1172 (1925).

[36] See Ley, H., and Arends, B., *Z. physik. Chem.*, **B17**, 177 (1932); Vlès, F., and Gex, M., *Compt. rend.*, **180**, 1342 (1923).

[37] Noyes, W. A., Jr., and Kouperman, A. B , *J. Am. Chem. Soc.*, **45**, 1398 (1923); Wobbe, D. E., and Noyes, W. A., Jr., *Ibid.*, **48**, 2856 (1926).

[38] Benton, A. F., and Cunningham, G. L., *J. Am. Chem. Soc.*, **57**, 2227 (1935).

[39] Allmand, A. J., and Reeve, L., *J. Chem Soc.*, 2834 (**1926**).

[40] Baur, E., believes there is a direct decomposition into carbon monoxide, carbon dioxide and water. *Z. physik. Chem.*, **111**, 315 (1924).

[41] Winther, C , and Oxholt-Howe, H., *Z. wiss. Phot.*, **14**, 196 (1914).

[42] Kunz-Krause, H., and Manicke, P., *Ber. Pharm. Ges.*, **32**, 209 (1922).

[43] Padoa, M., and Vita, N., *Gazz. chim. ital.*, **54**, 147 (1924); see also *Atti Cong. naz. chim. pura applicata*, 398 (1923).

$$[\mathrm{Co(C_2O_4)_3}]''' + h\nu \longrightarrow [\mathrm{CO(C_2O_4)_2}]'' + (\mathrm{C_2O_4})'$$
$$[\mathrm{Co(C_2O_4)_3}]''' + (\mathrm{C_2O_4})' \longrightarrow (\mathrm{C_2O_4})'' + 2\mathrm{CO_2} + [\mathrm{Co(C_2O_4)_2}]''$$

In most complex oxalates, Bhagwat [47] found the quantum yield to be two. He assumes the formation of an activated molecule as the primary process. On collision of this activated molecule with an unexcited molecule, both are decomposed. Potassium cuprioxalate requires a sensitizer in visible light. The decomposition products include copper, cuprous oxide, carbon monoxide and carbon dioxide. The quantum yield is 0.66. Bhagwat makes the assumption that the molecule absorbs two quanta before being further activated through the sensitizer. The sensitizers employed by Dube and Dhar [48] were ferric chloride or uranyl nitrate. The reaction was of zero order. Increasing the amount of the sensitizer increased the rate through a maximum. The reaction was more effectively retarded by oxygen than by carbon dioxide. It was accelerated by the presence of a large excess of potassium oxalate.

Potassium manganioxalate absorbs light throughout the visible, with a maximum at about 4870A. Ghosh and Kappanna [49] find white light to more than treble the velocity of thermal decomposition of the potassium complex. The quantum yield is one when plane polarized light is used. Addition of oxalic acid diminishes the velocity of the reaction.

Allmand and Webb [50] found in the photodecomposition of $K_3Fe(C_2O_4)_3$, that the quantum yields, which decrease with increasing wave-length, are of the order of unity. The presence of potassium oxalate caused a slight decrease in the quantum yield, but all other electrolytes tested increased the yield slightly. Experiments with mixed light with varying proportions of two or three mercury arc lines, showed an amount of decomposition 25 to 30 per cent greater than that calculated on the basis of an additivity of their separate effects. On the other hand, the use of a continuous band between 3900 and 4600A caused a degree of decomposition about 20 per cent lower than that expected on the basis of additivity. The effects of intermittent and continuous exposures were the same. The quantum yield was independent of the intensity of the line 3650A (in some experi-

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[44] Berger, G., *Rec trav. chim.*, **44,** 47 (1925), Jaeger, M, and Berger, G, *Proc. K. Akad. Wetensch. Amsterdam.*, **23,** 84 (1920); *J. Chem. Soc.*, **118,** ii, 725 (1920)

[45] Bhagwat, W V., and Dhar, N. R., *Z. anorg. Chem*, **197,** 18 (1931); *Brit. Chem. Abs*, **1931A,** 579

[46] Murgulescu, I G., *Bul. soc. stiinte Cluj*, **8,** 193 (1935); *Chem. Abs.*, **30,** 4402 (1936).

[47] Bhagwat, W. V., *Z. anorg. allgem. Chem.*, **218,** 365 (1934); *Chem. Abs.*, **28,** 6636 (1934).

[48] Dube, H. L., and Dhar, N. R., *J. Phys. Chem.*, **36,** 626 (1932).

[49] Ghosh, J. C., and Kappanna, A. N., *Quart. J. Indian Chem. Soc.*, **3,** 127 (1926); *Brit. Chem. Abs.*, **A,** 1014 (1926).

[50] Allmand, A. J., and Webb, W. W., *J. Chem. Soc.*, 1518, 1531 (**1929**).

ments 4050A) over a range of fifteen to one, whether continuous or intermittent. These results tended to confirm the work of Padoa and Vita (see Chapter 12). They suggested that the primary result of the absorption of a light quantum is the activation of the ferrioxalate ion, a process regarded as involving the partial dislocation of the union between the ferric ion and one of the attached oxalate ions. Reaction then occurs on collision of such an activated ion with a normal ion. More recently, Allmand and Young [51] confirmed the synergistic action of two monochromatic rays and showed that the temperature coefficient for this reaction is "negative." They also observed that in aqueous solutions, the velocity of the photoreduction of ferric chloride by oxalic acid is proportional to the intensity, that the ferric ion has no effect other than a slight light filter effect, and that the quantum efficiency is of the order of unity.[52] Kornfeld and Mencke [53] had found the velocity proportional to the square root of the intensity of light in the blue, green, and violet and, within limits, independent of the concentration of the reagents. It varies with the duration of the reaction and rapidly tends to drop to zero. Addition of ferrous sulfate retards the reaction at a rate proportional to the concentration of the sulfate.

The decomposition of oxalic acid can also be sensitized to light by chromium and by uranyl salts, the latter being about three times as effective as the former.[54] The reaction in the presence of uranyl salts has been suggested for standardizing light sources employed in determination of the light fastness of dyes.[55] Büchi,[56] who finds the quantum yield to be unity, attributes the reaction to the decomposition of the non-ionized molecules of uranyl oxalate ($UO_2C_2O_4$) or of the complex ions $(UO_2(C_2O_4)_2)''$, since the rate is only independent of the oxalic acid concentration when the latter is equimolar with or greater than the uranyl salt.

Müller [57] disagrees with the theory of the formation of a sensitizer-complex molecule and attributes the decomposition to collisions of the second kind between activated uranyl ions and oxalic acid molecules or oxalate ions. Pierce [58] confirmed Bruner and Kozak [59] and Bacon [60] in finding a temperature coefficient of unity, but was unable to decide between the mechanisms involving a sensitizer-complex and that of Müller. Pringsheim [61] discards the theory of collisions with activated molecules because he finds the inhibiting effect of iodide ions on the photolysis too small in comparison with their effect on fluorescence. He therefore favors complex formation. The solution must not be alkaline when intended for use in an actinometer. The application of the reaction for this purpose has been discussed in Chapter 7, where more recent quantum yield measurements are mentioned.

The Eder Reaction. A reaction formerly employed in actinometry, but really too complex and too subject to the presence of accelerating and inhibiting impurities, is the Eder reaction.[62] A solution containing mercuric chloride and ammonium oxalate is employed. On exposure to light, the decomposition products of the oxalate were thought to bring about the reduction of the mercury salt to calomel. Winther[63] found that the sensitiveness of the solution to visible light depended upon the presence of traces of a ferric salt. The rate of deposition of calomel was proportional to the iron content provided this did not exceed a very low value. An excess of ferric salt, however, retarded the reaction, particularly in the absence of dissolved oxygen. Furthermore, highly purified solutions were still decomposed by ultraviolet light, although not markedly by visible light.

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[51] Allmand, A. J., and Young, K. W., *J. Chem. Soc.*, 3079 (1931).

[52] See also Baur, E., Ouellet, C., and Wackerlin, E., *Z. wiss. Phot*, **30**, 88 (1931); *Chem. Abs.*, **26**, 3729 (1932).

[53] Kornfeld, G., and Mencke, E., *Z. Elektrochem.*, **34**, 598 (1928).

[54] Landau, M., *Compt. rend.*, **156**, 1894 (1913); Mathews, J. H., and Dewey, L. H., *J. Phys. Chem.*, **17**, 211 (1913); Boll, *J. Chem. Soc.*, **108**, ii, 123 (1925); Kunz-Krause, H., and Manicke, P., *Ber. pharm. Ges.*, **32**, 209 (1922); Sandonnini, C., *Atti accad. Lincei*, **2**, 427 (1925); *Chem. Abs.*, **20**, 1018 (1926).

[55] Holmes, W. C., *Amer. Dyestuff Rep.*, **13**, 188, 197 (1924); *Chem. Abs.*, **18**, 1614 (1924).

[56] Büchi, P. F., *Z. physik. Chem.*, **111**, 269 (1924); *Chem. Abs*, **19**, 1097 (1925); Baur, E., *Z. physik. Chem.*, **111**, 315 (1924).

[57] Müller, R. H., *Proc. Roy. Soc.*, **121A**, 313 (1929).

[58] Pierce, W. C., *J. Am. Chem. Soc.*, **51**, 2731 (1929).

[59] Bruner, L., and Kozak, J., *Z. Elektrochem.*, **17**, 355 (1911).

[60] Bacon, R. E., *Philippine J. Sci.*, **2**, 129 (1907); **5**, 281 (1910).

[61] Pringsheim, P., *Physica*, **4**, 733 (1937); *Chem. Abs.*, **31**, 8380 (1937).

Comparative experiments by Winther and Oxholt-Howe,[64] in which equal volumes of the filtrate from the calomel formed in a previous exposure and a fresh solution of the same composition were exposed to the influence of light under similar conditions, indicate that the initial photochemical action leads to the formation of some substance which acts as a powerful negative catalyst. This is also observed in the case of a purified Eder's solution to which eosin has been added as a sensitizer to the visible. In general, the effect becomes more marked as the intensity of the light increases. There is an appreciable loss of sensitivity if the eosin solution has been insolated before having been added to the Eder's solution. Velocity measurements of these reactions have been made by Shpolskiĭ and Ivanova.[65]

Padoa and Minganti[66] have measured the temperature coefficients of the reaction at various wave-lengths. The reaction in green light was very slow and a small proportion of a dilute aqueous solution of tetrabromofluorescein was added as a sensitizer; the latter was also employed in some experiments with white light. The results were as follows: white light, 1.29; ultraviolet, 1.05; dark blue, 1.21; green with sensitizer, 1 75; white light with sensitizer, 1.50. Here it is apparent that the longer the wave-length, the higher the temperature coefficient. The effect of the sensitizer in raising the temperature coefficient with white light is attributed to the fact that the sensitizer gives preponderance to the action of the yellow and green rays, which have little activity when no sensitizing agent is present.

Trifonov[67] found that potassium mercuric oxalate can be decomposed by water and by light. Various workers, including Ghosh and Rangcharya,[68] have advanced evidence, in some cases spectrographic, for the formation of an intermediate compound in Eder's solution. Cartledge and Djang[69] find cobaltous salts alone to be much less effective in inducing the reaction than are ferrous salts. The former affect chiefly the dark reaction. The effect of the cobaltioxalate complex ion is essentially a pure catalysis in the light. The inhibiting effect of oxygen is greatest with the catalyzed photolysis, less with that which is uncatalyzed and least on the photolysis of the cobaltioxalate ion alone.[70]

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[62] Krauss, F., and Berge, K., *J. Prakt Chem*, **136**, 257 (1933); see also Bekhterev, P., *J. Russ. Phys.-Chem. Soc.*, **57**, 161 (1925); *Chem. Abs*, **20**, 2459 (1926); Pitzer, E. C, Gordon, N., and Wilson, D., *J. Am. Chem. Soc.*, **58**, 67 (1936); Wieland, H., and Zilg, W., *Annalen,* **530**, 1656 (1937); *Chem. Abs.*, **32**, 1656 (1938).

[63] Winther, C., *Z. wiss. Phot.*, **8**, 135, 197 (1910); **14**, 172 (1914); Berger, G., *Rec. trav. chim.*, **40**, 387 (1921); *Chem. Abs.*, **16**, 1175 (1922)

[64] Winther, C., and Oxholt-Howe, H., *Z. wiss. Phot.*, **13**, 89 (1913), *J. Chem. Soc.*, **106**, II, 10 (1914).

[65] Shpolskiĭ, E., and Ivanova, E. N., *J. Phys Chem. (U.S.S.R.)*, **6**, 133 (1935), *Nature*, **16**, 647 (1930); *Chem. Abs.*, **29**, 7809 (1935). For the effect of oxygen, see Shpolskiĭ, E., and Iljina, A., *Acta Physicochim. U.R.S.S.*, **3**, 269 (1935); *Brit. Chem. Abs.*, **A**, 1214 (1936).

[66] Padoa, M., and Minganti, T., *Atti accad. Lincei,* **24** (V), ii, 97 (1915), *J. Chem. Soc.*, **108**, (ii), 719 (1915).

[67] Trifonov, N., *Mit. wiss.-tech. Arb. Republ. (Russ.)*, **13**, 72 (1924), *Chem Zentr.*, 382 (**1925**).

[68] Ghosh, J. C., and Rangcharya, T. L K., *J. Indian Chem. Soc.*, **5**, 569 (1928).

[69] Cartledge, G. H., and Djang, T. G., *J. Am. Chem. Soc.*, **55**, 3214 (1933).

Air, oxygen, hydrogen peroxide and ozone each inhibit the Eder reaction when the latter is carried out in the light of the carbon arc.[71] The same is true of the reduction of ferric oxalate. Roseveare and Olson[72] and Oberhauser and Schormüller[73] consider the Eder reaction a chain reaction. Phenols also strongly depress the reaction, an effect attributed by Weber[74] to a deactivation of the activated molecules or ions which form in the primary process. The same is true also of the eosin-sensitized reaction. When the solutions are saturated with oxygen, however, the phenols can depress the reaction only by acting as internal filters. Weber also believes the photosensitive component of the (unsensitized) solution to be a complex compound.

In the presence of eosin and with approximately monochromatic light of wave-length 5200A, 5460 or 5760A, there is a short induction period, after which the reaction proceeds linearly with time.[75] The speed of reaction is proportional to the intensity of light, both in the case of white light and of monochromatic illumination. In the concentration interval 5×10^{-7} to 5×10^{-5} gm. per cc., the speed increases in proportion to the concentration, but between 3×10^{-5} and 10^{-4} gm. per cc. the speed is constant. At higher concentrations, the rate begins to decrease. The decrease of sensitization as well as the damping of fluorescence as functions of the concentration begin from the same sharp threshold. The rate of the reaction is proportional to the concentration of mercuric chloride and, above concentrations of 0.01 gm. per cc., is independent of the concentration of oxalate. Between 15° and 5°, the temperature coefficient is 2.6 and between 25° and 15°, 1.9. The energy of activation is between 10 and 15 kcal. Beginning at 30°, the dark reaction acquires a noticeable speed. For the wave-lengths 5470 and 5760A, the quantum yield was, in the presence of oxygen, 12.5, a correction being made for the energy lost as fluorescence.[76]

Reaction Between Iodine and Potassium Oxalate in Aqueous Solution. The photochemical reaction between iodine and potassium oxalate

$$I_2 + C_2O_4'' \longrightarrow 2I' + 2CO_2$$

has been the subject of much study.[77] Berthoud and Bellenot showed that the rate of reaction is proportional to the concentration of the oxalate ion and inversely to the concentration of the iodide ion. The latter exerts a retarding effect. The rate is also proportional to the square root of the light intensity and to a power of the titratable iodine concentration which varies between 0.5 and −0.5 depending upon the completeness of the absorption of the light, that is, upon the wave-length. When absorption is weak, as it is when red light is employed, the rate is directly proportional to the square root of the iodine concentration but when absorption is complete as in blue light, the rate is inversely proportional to the square root of the iodine concentration. The results of Berthoud and Bellenot on the relation of the rate to the intensity were subsequently confirmed by others, who varied the intensity by more adequate methods than their sector device.[78] Bhagwat [79] believes this square root relation is not constant when the rate is varied over wide limits. Dhar, Bhattacharya and Mukerji [80] find the relation between the velocity and the light intensity to vary from one-third to approximately five-fourths when the wave-lengths employed are in the range 3340 to 8750A.

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[70] Cartledge, G. H , and Goldheim, S. L., *J. Am. Chem. Soc.*, **55**, 3583 (1933) have attempted a determination of the nature of the complexes formed in Eder's solution.

[71] Dunnicliff, H. B., and Joshi, J. N., *J. Indian Chem. Soc.*, **6**, 121 (1929); *Chem. Abs.*, **23**, 2887 (1929).

[72] Roseveare, W. E , and Olson, A R , *J. Am Chem. Soc.*, **51**, 1716 (1929); **52**, 2617 (1930).

[73] Oberhauser, F., and Schormüller, J., *Annalen*, **470**, 111 (1929)

[74] Weber, K , *Z. physik. Chem.*, **A169**, 224 (1934).

[75] Shpolskiĭ, E. V., and Kolesnikova, N. I., *J. Phys. Chem. (U.S S R)*, **5**, 1199 (1934); *Chem. Abs.*, **29**, 6145 (1935); *Brit. Chem. Abs.*, **A**, 809 (1936).

[76] For an analogous reaction between mercuric chloride and malic acid in the presence of various sensitizers, see Baur, E., *Helv. Chim. Acta*, **20**, 974 (1937).

[77] Mukerji, B. K., and Dhar, N. R , *Z physik. Chem.*, **120**, 75 (1926); *Z. Elektrochem.*, **31**, 621 (1925); *Trans. Faraday Soc.*, **21**, 489 (1926); Berthoud, A., and Bellenot, H., *Helv. Chim. Acta*, **7**, 304 (1924); *J. Chim. Phys.*, **21**, 308 (1924).

Berthoud and Bellenot accounted for their results in either red or blue light by a mechanism which involved the assumption that light dissociates iodine molecules but not the triiodide ion predominantly present in the solutions, which contained an excess of potassium iodide. Their mechanism involved the chain reactions

$$\begin{gathered} I + C_2O_4'' \longrightarrow I' + C_2O_4' \\ C_2O_4' + I_2 \longrightarrow 2CO_2 + I' + I \end{gathered}$$

and the chain-breaking reactions

$$\begin{gathered} 2I + I' \longrightarrow I_3' \\ I + I \longrightarrow I_2 \end{gathered}$$

From these reactions and the assumption of stationary states for the concentrations of iodine atoms and C_2O_4', it was possible to attain agreement with the experimental results for the reaction rates under varied conditions. They found quantum yields of 0.11 (4860A) with respect to the total energy absorbed or 3.2 with respect to that absorbed by I_2. With blue light larger values, quantum yields up to 25 were obtained, verifying the chain nature of the reaction.

The temperature coefficients determined by Allmand and Young and by the Indian workers were high, about 3.0; those of the thermal reaction were as high as 6.86. This indicated a high energy of activation for some partial process, a feature difficult to reconcile with the chains proposed by Berthoud and Bellenot. Other reactions of iodine solutions required the concept that the triiodide ion present is photochemically decomposed with the production of iodine atoms and possibly the hypothetical ion I_2'. It was found possible by Dickinson and Ravitz [81] to derive a mechanism from this concept of the primary process which also led to the experimental results of Berthoud and Bellenot. Such a mechanism was employed by Allmand and Young, who appended to their paper a discussion of the application of the mechanism to other photochemical oxidations by iodine. This mechanism has also been used by Griffith, McKeown and Winn [82] in their treatment of the analogous reactions between bromine and potassium oxalate. They conceived the action of the free halogen to be only that of an internal light filter. In their experimental work they considered also the case in which there is but little of the iodide ion in excess. Berthoud,[83] however, has reiterated that it is the iodine molecule which is dissociated.

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[78] Briers, F., Chapman, D. L., and Walters, E., *J. Chem. Soc.*, **129,** 562 (1926); Allmand, A. J., and Young, K. W., *Trans. Faraday Soc.*, **27,** 515 (1931).

[79] Bhagwat, W. V., *J. Indian Chem. Soc.*, **10,** 649 (1933), *Brit. Chem Abs.*, **1934A,** 156; *Chem. Abs.*, **28,** 1928 (1934).

[80] Dhar, N. R., Bhattacharya, A. K., and Mukerji, B., *Nature*, **131,** 840 (1933); *J. Indian Chem. Soc.*, **12,** 151 (1935); *Brit Chem. Abs.*, **1935A,** 832; *Chem Abs.*, **29,** 5351 (1935).

[81] Dickinson, R. G., and Ravitz, S. F., *J. Am. Chem. Soc.*, **52,** 4770 (1930).

[82] Griffith, R. O., McKeown, A., and Winn, A. G., *Trans. Faraday Soc.*, **29,** 369, 386 (1933).

[83] Berthoud, A., *Helv. Chim. Acta*, **16,** 393 (1933).

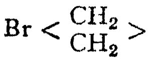
Abel and Schmidt[84] have found evidence for the occurrence of the intermediary compound, probably C_2O_4', the existence of which had been assumed in the earlier mechanisms and for which kinetic evidence had been given by Abel, Schmidt and Retter.[85] Its long life is indicated by an initial reaction rate increase and by the photochemical after-effect which had been studied by the intermittent sector method by Berthoud. (See Chapter 15.)

It may also be noted that Bhattacharya and Dhar[86] have proposed that the analogous bromine-oxalate reaction may proceed by way of excited molecules, since they believe it can be markedly accelerated by wave-lengths in the region of 7304A.

Malonic and Other Acids. The products of the photodecomposition of malonic acid, either in the presence or absence of uranyl sulfate, are acetic acid and carbon dioxide.[87] With 0.01 molar uranyl sulfate, the rate decreases with decreasing concentrations of malonic acid, being approximately proportional to the cube root of the concentration of the latter. In the absence of catalyst, the quantum yield varies between 0.68 and 0.81, being little affected by the wave-length. In the presence of catalyst it is lower, 0.27. The extent of ionization of the malonic acid does not affect the results. There may be two independent reactions, one due to the light absorbed by the malonic acid and the other to that absorbed by the catalyst, but there is no evidence for the formation of a complex between malonic acid and uranyl salts. The mechanism of the catalyzed reaction may involve the deactivation of excited uranyl sulfate molecules by collision with other uranyl sulfate or with malonic acid molecules. The temperature coefficient of the sensitized reaction is 1.13,[88] and that of the unsensitized reaction, 1.07.[89] Malonic anhydride (carbon suboxide, C_2O_3) is not appreciably affected by ultraviolet light.[90]

Coster and van der Ziel[91] have noted in the photochemical decomposition of monoalkylmalonic acids the formation of a substance that is not a fatty acid. This conclusion was drawn from study of its x-ray spectrum.

A uranyl salt-photosensitized reaction between succinic acid and methylene blue at 3600A is, after an initial induction period, of zero order with respect to the methylene blue. The rate is proportional to the incident intensity and independent of the pH. One-half of the collisions between excited uranyl ions and succinic acid molecules are believed to be effective.[92]

Sattler and Nicolet[93] find treatment of diethyl cyclopropane-1,1-dicarboxylate with bromine at 40° to 50°C. under mercury arc irradiation through quartz gives both  $Br < \genfrac{}{}{0pt}{}{CH_2}{CH_2} > C(COOC_2H_5)_2$ and $Br\,CH_2{\cdot}CH_2{\cdot}CBr{\cdot}(COOC_2H_5)_2$, with relatively larger amounts of the latter than when no irradiation is used. Stoermer and Ladewig[94] discovered that when alcoholic solutions of *trans*-cyclopentane-1,2-dicarboxylic acid are exposed to the Uviol lamp, conversion into mono- and di-esters occurs. The expected transformation into the *cis* modifications did not take place.

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[84] Abel, E., and Schmidt, H., *Naturwiss.*, **23**, 501 (1935).

[85] Abel, E., Schmidt, H., and Retter, K., *Z. physik. Chem.*, **163A**, 53 (1932); see also for the after-effect in the reaction between iodine and oxalic acid, Abel, E., Jokisch, R. Larisch, L., and Sassmann, H., *Z. Elektrochem.*, **43**, 629 (1937).

[86] Bhattacharya, A. K., and Dhar, N. R., *J. Indian Chem. Soc.*, **6**, 523 (1929); *Chem. Abs.*, **24**, 1033 (1930); Bhattacharya, A. K., Prakash, O., and Dhar, N. R., *Z. anorg. allgem. Chem.*, **196**, 26 (1931); **209**, 139 (1932).

[87] Pierce, W. C., Leviton, A., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **51**, 80 (1929).

[88] Pierce, W. C., *J. Am. Chem. Soc.*, **51**, 2731 (1929).

[89] Pierce, W. C., and Morey, G. H., *J. Am. Chem. Soc.*, **54**, 467 (1932).

[90] Edwards, M. J., and Williams, J. M., *J. Chem. Soc.*, 856 (1927).

[91] Coster, D., and van der Ziel, A., *Z. physik. Chem.*, **B20**, 385 (1933).

[92] Ghosh, J C., Banerjee, T., and Bhatta, B., *Z. physik. Chem.*, **B32**, 163 (1936).

[93] Sattler, L., and Nicolet, B. H., *J. Am. Chem. Soc.*, **49**, 2066 (1927).

Oxalyl chloride is slowly decomposed when irradiated with wave-lengths shorter than 3800A, the reaction being predominantly monomolecular with a low quantum yield.[95] The final products are phosgene and carbon monoxide, but it is believed that the initial products are chlorine and carbon monoxide. Two mechanisms are proposed for the effects of different wave-lengths. With short ones, the molecule breaks at the carbon-carbon bond, but with longer wave-lengths, a break at one of the carbon-chlorine bonds predominates.

HYDROXYLIC ACIDS

Volmar[96] found that hydroxy-acids and their salts undergo photolysis under the influence of ultraviolet rays, and to a lesser extent in sunlight. Tartaric acid in 1-per cent solution after three hours gave 3.5 cc. of gas composed of carbon dioxide 66 per cent, carbon monoxide 10 per cent, hydrogen 21 per cent, and hydrocarbons 3 per cent. The solution contained aldehydes and small quantities of a reducing substance of the nature of a sugar. In the presence of alkalies, the carbon monoxide was lessened or absent, owing to condensation with a portion of the hydrogen with production of the aldehydic substances. The homologs of tartaric acid behaved similarly. The decomposition may be accelerated by the presence of catalysts such as uranyl acetate or iron salts.[97]

Winther[98] finds the oxidation of citric, tartaric, lactic and oxalic acids to be insensitive to light.

In the presence of tartaric, lactic or mandelic acids as oxygen acceptors, the photochemical reduction of ferric chloride is of zero order.[99] With both mandelic acid and lactic acid, the life period of the excited ferric ion is of the order of 10^{-9} second. With tartaric acid, the reaction is complicated by the circumstance that the immediate product of the photooxidation of the acid also reacts with ferric salts under the influence of light. In the case of mandelic acid, the quantum yield is unity at 4880A, but becomes nearly 1.4 at 3900A; with tartaric acid and lactic acid, it is nearly 0.5 at 4880A and 0.8 at 3900A. Oxygen has been found a negative catalyst in the photochemical oxidation of lactic acid by bromine water by Dunnicliff and Joshi.[100]

Lactic Acid. The decomposition of solid calcium lactate by ultraviolet light was found to give carbon monoxide, methane, ethane and hydrogen.[101] Baudisch[102] stated that lactic acid, repeatedly purified from its zinc salt, gave decisive reactions for acetaldehyde after about forty hours of irradiation followed by distillation. He could not detect methane, although Schanz had previously found a small amount.[103] Euler[104] had, however, previously shown that in pure aqueous solutions at 70°C., there were produced alcohol and a gas, the latter being 90 per cent carbon dioxide and 10 per cent a mixture of hydrogen and carbon monoxide. The rate did not appear to depend upon the concentration of the acid. An induction period of about two hours was noted. The rate of evolution of gas was not accelerated by the presence of either ferrous or ferric salts, although the latter were reduced.[105]

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[94] Stoermer, R., and Ladewig, H., *Ber.*, **47**, 1803 (1914).

[95] Krauskopf, K. B., and Rollefson, G. K., *J. Am. Chem. Soc.*, **58**, 443 (1936).

[96] Volmar, *Compt. rend.*, **176**, 742 (1923); *J. Chem Soc.*, **124**, (II), 279 (1923); *J.S C I.*, **42A**, 423 (1923).

[97] Neuberg, C., *Biochem. Z.*, **39**, 158 (1912)

[98] Winther, C., *Z. physik. Chem.*, **A174**, 41 (1935).

[99] Ghosh, J. C., and Purkayastha, R. M , *J Indian Chem. Soc.*, **6**, 827 (1929); *Chem. Abs.*, **24**, 2055 (1930).

[100] Dunnicliff, H. B., and Joshi, J. N., *J Indian Chem Soc.*, **6**, 121 (1929); *Chem Abs.*, **23**, 2887 (1929).

[101] Berthelot, D., and Gaudechon, H., *Compt. rend*, **151**, 478 (1910).

[102] Baudisch, O., *Biochem. Z.*, **103**, 59 (1920); *Chem. Abs.*, **14**, 2776 (1920).

Bredig, Mangold and Williams[106] state that inactive lactic acid is decomposed by light of wave lengths 2200 to 3000A, but is not rendered optically active. Bolin[107] found that no decomposition occurs in glass flasks.[108] Burns[109] found wave lengths less than 2500A effective in decomposing lactic acid in aqueous solution, the chief products being alcohol and carbon dioxide. The amounts of alcohol were 19 per cent in excess of those required by the assumption that the products are equal amounts of alcohol and carbon dioxide. The quantum yield, based on the carbon dioxide, was approximately 0.65, although the intensity measurements were admittedly inaccurate. Based upon the alcohol formed, it was 0.77. Carbon monoxide, 3.82 per cent of the total gas, saturated hydrocarbons, 5.36 per cent and unsaturated hydrocarbons 0.89 per cent, formed about 9 per cent of the gaseous products, but neither aldehyde nor hydrogen peroxide could be detected. Lieben, Löwe, and Bauminger[110] have stated that lactic acid in alkaline solutions yields acetaldehyde and acetic acid, possibly formed through pyruvic acid, which in alkaline solution they found to be more readily attacked than lactic acid. The reaction could be sensitized to diffused daylight by sodium anthraquinonesulfonate. Müller[111] found that in the presence of uranyl sulfate, lactic acid and sodium lactate could be photochemically converted into acetaldehyde with a quantum yield of approximately unity (4025A).

Ganassini[112] and Ciamician and Silber[113] found that lactic acid on prolonged exposure to sunlight in the presence of air yielded qualitative tests for acetic acid, pyruvic acid, acetaldehyde and carbon dioxide. Burns,[114] in extending his work to oxygen-containing solutions, noted the chief products to be carbon dioxide, acetaldehyde, a peroxide and acetic acid, thus confirming the results of Baudisch and of Neuberg if it were assumed that they had worked without excluding oxygen. Neither ethanol nor pyruvic acid could be detected.

Studies of the rate of the oxidation of mandelic acid by methylene blue in the presence of uranyl nitrate as photosensitizer have been made by Ghosh, Narayanmurti and Roy[115] at 4360, 3660, 3130 and 2540A. In each case, there were short induction periods, those at 3660A, and particularly 4360A, being longer. The results are complex. The photochemical oxidation of mandelic acid by bromine is of first order in the absence of potassium bromide and of zero order in its presence.[116]

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[103] Schanz, F., *Arch. ges. Physiol*, **170**, 650 (1918).

[104] Euler, H., *Arkiv. Kem Min. Geol.*, No 8, 1911; *J. Chem Soc.*, **102**, ii, 112 (1912). Euler, H., and Ryd, S. *Biochem. Z*. **51**, 97 (1913); Euler, H, and Lindberg, E, *Ibid.*, **39**, 410 (1912).

[105] See also Schanz, F., *Arch. ges Physiol.*, **170**, 650 (1918).

[106] Bredig, G, Mangold, P., and Williams, T G., *Z. angew. Chem.*, **36**, 456 (1923), *Chem Abs*, **17**, 3868 (1923).

[107] Bolin, I., *Z. physik. Chem.*, **87**, 490 (1914).

[108] For absorption data, see Dietzel, R., and Krug, R., *Arch. Pharm.*, **264**, 117 (1926).

[109] Burns, G. R., *J. Am. Chem. Soc.*, **51**, 3165 (1929).

[110] Lieben, F., Löwe, L., and Bauminger, B., *Biochem. Z.*, **271**, 209 (1934).

[111] Müller, R H, *Biochem. Z.*, **178**, 77 (1926).

[112] Ganassini, D., *Chem. Zentr.*, I, 387 (1913); I, 729 (1910); *Chem. Abs.*, **5**, 3236 (1911) from *Seduta soc. med. chir., Pavia,* 1909.

[113] Ciamician, G., and Silber, P., *Ber.*, **46**, 1558 (1913).

[114] Burns, G. R., *J. Am. Chem. Soc.*, **52**, 5272 (1930).

[115] Ghosh, J. C., Narayanmurti, D. S., and Roy, N. K., *Z. physik. Chem.*, **B29**, 236 (1935).

Ghosh and Bhattacharya[117] find that for monochromatic light, the rate constant is proportional to the square root of the absorbed energy. It was believed that the combined action of rays of two wave-lengths was less than that of the sum of their effects taken separately. For 4360A the quantum yield is 12.5, but it varies greatly with the light intensity and wave-length.

Ghosh and Ray[118] find the uranyl-sensitized oxidation of mandelic acid by bromine a chain reaction with high quantum yield.

Tartaric Acid. The formation of reducing substances and carbon dioxide when tartaric acid is exposed to ultraviolet rays was described by Euler and Ryd.[119] Ferric salts increase the rate of gas evolution, being themselves reduced.[120] In the presence of uranium salts, the α-hydroxy acids decompose slowly in sunlight into formic acid and the respective aldehydes and ketones.[121] Tartaric acid yields glyoxal and citric acid yields acetone. This photochemical reaction could be employed for the detection of tartaric acid in a solution of citric acid. It appeared specific in that it was not given by any of the other aliphatic hydroxy-acids examined by Pavolino. After the addition of a uranium salt, the solution to be examined is exposed for at least thirty minutes to sunlight or to a light source of similar intensity. A few drops of phenylhydrazine or a corresponding quantity of a 5 per cent solution of its acetate are added. If tartaric acid was originally present, a yellow precipitate of phenylglyoxal osazone formed. Its color soon changed to wine red, probably because of the oxidative effect of the uranium salt.

Volmar[122] finds that solutions of potassium antimonyl tartrate and the corresponding compounds of arsenic, bismuth, copper and iron undergo decomposition on exposure to ultraviolet radiation with liberation of the metal, the maximum effect being produced in the case of the bismuth compound. Potassium borotartrate is an exception; Volmer considers this due to the fact that it appears to be a mixture rather than a definite compound.

Light accelerates the direct air oxidation of sodium tartrate catalyzed by sodium sulfite, cerium hydroxide, sodium hydroxide, sodium carbonate or bicarbonate and ferrous hydroxide.[123]

The oxidation of citric acid by chromic acid has temperature coefficients of 3.8 in darkness and 1.05 in light. The velocity varies as the square root of the light intensity, although in the case of tartaric and lactic acids, the rate is directly proportional to the light intensity.[124]

In the case of citric acid, the process involves chains, the length of which increases with temperature and concentration.

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[116] Ghosh, J. C., and Purkayastha, R. M., *Z. physik. Chem.*, **7B**, 285 (1930); *J Indian Chem Soc*, **6**, 361 (1929).

[117] Ghosh, J. C., and Bhattacharya, S. K., *Z. physik. Chem*, **31B**, 420 (1936)

[118] Ghosh, J. C., and Ray, B. B., *Z. physik. Chem.*, **32B**, 158 (1936).

[119] Euler, H., and Ryd, S., *Biochem. Z*, **51**, 97 (1913).

[120] For data on the absorption spectra of tartaric acid solutions, see Bruhat, G., and Legris, R., *Compt. rend.*, **189**, 745 (1929); *Ann. Phys.*, **13**, 6 (1930); Descamps, R., *Compt rend.*, **185**, 116 (1927); Lucas, R., and Schwob, M., *Compt. rend.*, **192**, 225 (1931); Bruhat, G., *Compt rend.*, **192**, 489 (1931).

[121] Pavolino, T., *Giorn. farm. chim.*, **79**, 310 (1930); *Chem. Abs.*, **25**, 251 (1931).

[122] Volmar, *Compt. rend.*, **176**, 1465 (1923); *J. Chem. Soc.*, **124** (ii), 453 (1923).

[123] Palit, C. C., and Dhar, N. R., *J. Indian Chem. Soc.*, **11**, 471 (1934); *Chem. Abs.*, **28**, 6780 (1934).

[124] Bhattacharya, A. K., and Dhar, N. R., *Z. anorg. allgem. Chem.*, **169**, 381 (1928); *Chem. Abs.*, **22**, 2111 (1928); *Z. anorg. allgem. Chem.*, **196**, 26 (1931); *Chem. Abs.*, **25**, 2052 (1931).

KETO-ACIDS

Comparatively few photochemical studies have been made of the ketonic acids, although occasional use has been made of ultraviolet absorption studies in the solution of problems relating to their constitution.[125]

The yield of acetoin formed by ultraviolet light from aqueous solutions of pyruvic acid decreases from 100 per cent at 0.2 to 3 molar to 12 per cent at 11.4 molar.[126] In the presence of benzaldehyde, Discherl detected the formation of acetylphenylcarbinol. Benzaldehyde, benzene, salts and dehydrating agents hinder acyloin formation. The irradiation of 0.5 to 2 molar solutions of α-ketovaleric acid gave a 39 to 40 per cent yield of butyroin.

The photoöxidation of pyruvic acid is sensitized by eosin and isochlorophylline, slightly by rhodamine B and is inhibited by hydrogen cyanide. In alkaline solutions, oxalic acid is formed.[127] Lipmann[128] finds light to increase the reduction of methylene blue or of ferric ion by pyruvic acid. In the latter case, the pyruvic acid appeared to be oxidized to acetic acid and carbon dioxide.

When sensitized by eosin, chlorophyll, ferric or uranyl salts, the photochemical oxidation of glycolic acid yields formaldehyde and carbon dioxide, but glyoxylic acid gives only carbonic acid.[129] Ferric gluconate is reduced in sunlight to a ferrous salt.[130]

HALOGENATED ACIDS

Ultraviolet light splits aqueous solutions of halogenated fatty acids and their salts in various ways, among the products being formaldehyde, carbon dioxide, hydrogen, and chlorine.[131] Euler[132] found that the haloacetic acids split off their halogen in aqueous solutions at 18°C. in ultraviolet light at a rate comparable to that in darkness at 100°C. The rate decreased at higher concentrations of the acids.

In benzene solution, monochloracetic acid also lost some chlorine. Other products identified included a small amount of polyglycolide, fumaric acid and another unsaturated acid. Bromoacetic acid suffered decomposition more readily. Little is known of the mechanism by which the unsaturated acids were produced. In ether, qualitatively similar results were also reported with both monochlor- and monobrom-acetic acids. The reaction becomes evident when wave-lengths between 3130 and 2660A are employed. A quantum yield of unity at 2536A was reported by Rudberg[133] for monochloracetic acid. For monobromacetic acid, he found it only 0.34, but that this increased as the solution was made alkaline. More recently, Farkas[134] has reported for monochloracetic acid a quantum yield of 0.9, independent of the pH of the solution for wave-lengths less than 2300A. Dain and Puzenkin[135] employ the reaction for absolute actinometric measurements.

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[125] Pyruvic acid, Henri V., and Fromageot, C., *Bull. soc. chim.*, **37**, 845 (1925); Pascal, P., *Ibid.*, **39**, 396 (1926); Benzylmethylglyoxal, Lowry, T. M., Moureau, H., and MacConkey, C. A., *J. Chem. Soc.*, 3167 (**1928**); Levulinic acid, Gex. M., *Arch. phys. biol.*, **10**, 250 (1933); α-ketonic acids, Fromageot, C. Pelletier, M., and Ehrenstein, P., *Bull. soc. chim.*, **51**, 1282 (1932); β-ketogluconic acid, Niederhoff, P., *Z. physiol. Chem.*, **181**, 83 (1929).

[126] Discherl, W., *Z. physiol. Chem.*, **219**, 177 (1933); *Brit. Chem. Abs.*, **1933A**, 1037.

[127] Meyer, K., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 341 (1935); *Chem. Abs.*, **30**, 7457 (1936).

[128] Lipmann, F., *Skand. Arch. Physiol.*, **76**, 186 (1937); *Chem. Abs.*, **31**, 4904 (1937).

[129] Baur, E., *Helv. Chim. Acta*, **19**, 234 (1936).

[130] Neiger, R., and Neuschul, P., *Z. physik. Chem.*, **A177**, 355 (1936).

[131] Jaeger, F. M., and Berger, G., *Rec. trav. chim.*, **41**, 71 (1922).

[132] Euler, H., *Ber.*, **49**, 1366 (1916).

[133] Rudberg, E. G., *Z. Physik*, **24**, 247 (1924).

[134] Farkas, L., *Z. physik. Chem.*, **B23**, 89 (1933).

The photochemical reactions between the halo-acetic acids and alcohol were studied by Cassel,[136] who observed decomposition into the unsubstituted acid, acetic aldehyde and the halogen acid. Wave-lengths shorter than 2500A were required. The halogen could be more readily liberated by light from 1-bromosuccinic acid than from 1-chlorosuccinic acid.

A uranyl-sensitized photoöxidation of monochloracetic acid by potassium permanganate has been found of zero order with respect to the oxidant by Ghosh and Ray,[137] who employed the wave-lengths 3660 and 4360A. Its rate varies as the intensity of the incident radiation and is influenced by the sensitizer concentration.

Trichloracetic acid decomposes into carbon dioxide and chloroform, the temperature coefficient being 3.6 in light and 4.28 in darkness, according to Banerji and Dhar.[138] The quantum yields are abnormally high and increase with the temperature and the frequency of the incident radiation.[139] Solutions in water show some absorption of visible light which is without much photochemical effect, although water acts as photosensitizer. Absorption begins to increase at 3200A, is complete at 3000A, and decreases at shorter wave-lengths.

UNSATURATED ACIDS

The stereoisomeric transformations of unsaturated dicarboxylic acids, direct and sensitized, have been much studied. Kailan[140] found that solid fumaric acid was not converted into maleic acid by ultraviolet light, and that maleic acid could be converted into fumaric only to the very slightest extent. But in aqueous solutions (about 0.084 normal), an equilibrium between the two acids could be reached from either side. The equilibrium was displaced somewhat toward the side of maleic acid with increasing concentrations. At 45° to 50°C., with $0.1N$ solution the equilibrium mixture contained 75 per cent of maleic acid and in $0.4N$ solution 79 per cent. The velocity of transformation was much greater in quartz than in glass vessels, but the equilibrium composition was the same.

Earlier observations were recorded by Stoermer with Frederici, Brautigam and Neckel,[141] who found that although fumaric acid when irradiated yielded about 70 per cent of maleic acid, sodium fumarate could not be converted into sodium maleate in this manner. The transformation of fumaric acid into maleic acid could also be effected in benzene solution.[142] Stoermer, who has made extensive investigations of the stereoisomeric transformations of ethenoid linkages in a wide variety of compounds, showed that at photochemical equilibrium, the less stable form was present in the larger amount, proving that light does not act merely as a catalyst in hastening a thermal equilibrium.

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[135] Dain, B. Y., and Puzenkin, E. S., *Ber. ukrain. wiss. Forsch-Inst physik. Chem.*, **4**, 75 (1934); *Chem. Abs.*, **29**, 2451 (1935).

[136] Cassel, H. W., *Z. physik. Chem.*, **92**, 113 (1916).

[137] Ghosh, J C, and Ray, B. B., *J Indian Chem. Soc.*, **13**, 1 (1936); *Chem. Abs.*, **30**, 4093 (1936).

[138] Banerji, S. N, and Dhar, N. R, *Z. anorg. allgem. Chem.*, **134**, 172 (1924); *Chem. Abs.*, **18**, 2634 (1924).

[139] Bhattacharya, A. K., and Dhar, N. R., *Z. anorg. allgem. Chem*, **209**, 123 (1932); *Chem. Abs.*, **27**, 907 (1933)

[140] Kailan, A., *Z. physik. Chem.*, **87**, 333 (1914); *J. Chem. Soc.*, **106** (ii), 449 (1914); *Monatsh.*, **41**, 305 (1920); *Chem. Abs.*, **15**, 1100 (1921).

[141] Stoermer, R., with Frederici, Brautigam, and Neckel, *Ber.*, **44**, 637 (1911).

[142] Stoermer, R., *Ber.*, **42**, 4865 (1909); *J. Chem. Soc.*, **98** (ii), 114 (1910).

Warburg[143] measured the quantum yields for the transformation of each stereoisomer at the wave-lengths 2070, 2530 and 2820A. The yields were but little affected by the change in wave-length, being slightly greater at 2530A than at either of the other two. For the conversion of maleic into fumaric acid, the values ranged from 0.032 to 0.049, being slightly greater at lower (0.00514) than at higher (0.0102) concentrations. For the reverse transformation of fumaric into maleic acid, the yields were about twice as great, varying from 0.08 to 0.133. In this case, the higher values were obtained in the more concentrated solutions. The low quantum yields were assumed to be due to the fact that after the initial excitation of the molecule, it tends on collision to return to the original form more frequently than it does to yield the isomer. At 3130A, Vaidya[144] found the quantum yields for maleic acid to be at 0.01 molar, 0.048, at 0.005 molar, 0.052 and for fumaric acid, 0.117 and 0.083, respectively.

Absorption data for maleic and fumaric acids, their *l*-menthyl and dimethyl esters and maleic anhydride in various solvents were given by Wassermann and Smakula[145] over the range 3000 to 1900A. Their data were thought not to eliminate the Anschütz cyclic formula for maleic acid.

It has been suggested that maleic and fumaric acids may have a common excited electronic state.[146] Olson[147] has given a theoretical treatment of the conversion. The potential energy wells corresponding to the separate acids are separated by a potential barrier, so that the transformation cannot occur thermally at ordinary temperatures. Olson plotted curves of the potential energy against the angle through which one half of the molecule is twisted relative to the other about the double bond as axis. Such curves for the excited state make evident the manner in which the stabilizing effect of the double bond disappears on excitation of one of the electrons of the bond. From these curves Olson determined by the methods of wave mechanics, the probabilities that on the return of the molecule from the excited state, the *cis* or the *trans* form would result. With Hudson, Olson[148] further developed methods for predicting from the extinction coefficients of the acids at various concentrations and wave-lengths, the compositions of the photostationary states when the acids, in several concentrations, are irradiated with various monochromatic wave-lengths. From thermal data, calculations of the heats of isomerization were also made.

Comparison of the absorption spectra of the *cis* and *trans* forms of a number of related stereoisomeric compounds usually show that of the more stable *trans* form to lie closer to the visible. Contrary to this general rule, in the three pairs of compounds, diethyl αα′-diphenylfumarate and maleate, dimethyl αα′-di-*m*-tolylfumarate and maleate, and dimethyl αα′-di-*p*-tolylfumarate and maleate, the absorption curve of the *cis* form is the closer to the visible, and is, therefore, the more stable form at low temperatures. Ramart-Lucas and Hoch[149] prepared these three fumarates by the irreversible action of ultraviolet on the corresponding maleates; this reaction gave, in addition, carbalkoxyarylindones, also formed by the action of ultraviolet light on the dialkyl αα′-diarylfumarates. Irradiation of the sodium salts of the $\alpha\alpha'$-diarylmaleic acids with ultraviolet light gave the sodium salts of the arylindonecarboxylic acid.[150]

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[143] Warburg, E., *Sitzb. Preuss. Akad. Math.-Phys*, 960 (1919); *Chem. Abs.*, 14, 1931 (1920).
[144] Vaidya, B. K., *Proc. Roy. Soc.*, A129, 299 (1930).
[145] Wassermann, A., and Smakula, A., *Z. physik. Chem.*, A155, 366 (1931).
[146] Bonhoeffer, K. F., and Harteck, P., "Grundlagen der Photochemie," Dresden, Steinkopff, 270, 1933.
[147] Olson, A. R., *Trans. Faraday Soc.*, 27, 69 (1931).
[148] Olson, A. R., and Hudson, F. L., *J Am. Chem. Soc.*, 55, 1413 (1933).
[149] Ramart-Lucas, Mme., and Hoch, J., *Compt. rend.*, 189, 696 (1929).

The possibility of the photodissociation of the unsaturated acids into carbon dioxide and acids of the acrylic series has been discussed. Volmar[151] found that unsaturated dibasic acids undergo photolysis more rapidly than their saturated analogs. That of the *cis* compounds was five to six times as rapid as that of the *trans* forms, the latter behaving like monobasic acids. In the *cis* acids, the carboxyl groups were thought to exert a mutually enhancing effect. Itaconic acid behaved like succinic acid. On prolonged exposure to ultraviolet light, both the *cis* and *trans* forms behave alike after an equilibrium state has been set up. Olson and Hudson found that such photolyses occur with insufficient speed to interfere with their determinations of the stationary states resulting from stereoisomeric transformations.

Berezovskaya, Kogon and Moskalenskaya[152] found that light alone induced only the stereoisomeric changes in maleic and fumaric acids, but that the combined action of ultraviolet light and platinum led to decomposition. The barium salt of fumaric acid reacted similarly to the free acid, but the barium salt of maleic acid underwent no decomposition under these conditions.

The sensitization of the maleic-fumaric conversion to visible light by bromine, described by Wislicenus in 1895, has been extensively studied by Eggert and co-workers.[153] The ethyl esters were studied in carbon tetrachloride solution. The rate was proportional to the number of quanta absorbed, independent of the bromine concentration within the limits of 1 : 9, and independent of the carbon tetrachloride concentration within the limits 1 : 5. At 21°C., with the bromine concentration 0.1N, at the wave-length 4360A the quantum yield for the transformation was high, 295. At the same time, some of the bromine was photochemically added to the ester, the quantum yield for this reaction being 8.2.[154] These yields were independent of the intensity of the light and the concentration of the ester from pure ester to 70 moles of solvent per mole of ester. They were also independent of the bromine concentration from 0.03 to 0.3N. The intermediary formation of diethyl dibromosuccinate was postulated but no attempt was made to isolate it. Subsequent determinations by Wachholtz[155] at this wave-length showed, at various bromine concentrations, a range of from 108 to a maximum of 755 for the quantum yield for the transformation to fumarate. At 5570A the range was 77 to 307. The temperature and the wave-length employed were the chief determining factors. At the shorter wave-length (4360A) the yield increased approximately from 100 at 0° to 700 at 23°C.; at 5570A from 100 at 16° to 300 at 23°C. Similarly, the yields for the addition reaction depended only upon the temperature, wave-length and bromine concentration, values within the range of 3 to 42 being obtained. Bromine atoms, produced by photodissociation, form a complex short-lived intermediary product. This is considered a radical, since only one bromine atom is present. In a subsequent collision, the bromine atom is again liberated and fumarate formed. The liberation of the bromine permits it to act upon another maleate molecule and so accounts for the very high quantum yields. In the event of a collision of the radical with a bromine molecule, it is possible that dibromosuccinic ester may be formed with liberation of a bromine atom.

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[150] See also Biquard, D., *Ann. Chim.*, **20**, 97 (1933), for the change of methyl diphenylmaleate to the fumarate on irradiation of its alcoholic solution, catalyzed by a trace of bromine.

[151] Volmar, *Compt. rend.*, **181**, 467 (1925).

[152] Berezovskaya, F. I., Kogon, M., and Moskalenskaya, E., *Compt. rend. acad. sci. U.R.S.S.*, **4**, 50 (1934); *Chem. Abs.*, **29**, 2089 (1935).

[153] Eggert, J., *Physik. Z.*, **24**, 504 (1923); *Chem. Abs.*, **18**, 3548 (1924).

[154] Eggert, J., Wachholtz, F., and Schmidt, R., *Physik. Z.*, **26**, 865 (1925).

[155] Wachholtz, F., *Z. physik. Chem.*, **125**, 1 (1927).

In the case of the methyl ester (and also of the free acids), the quantum yields of the transformation and addition reactions are independent of the variation of the ester concentration and of the radiation intensity at high concentrations. At low concentrations, however, the yield for the isomerization decreases with decreasing ester concentration and with increasing intensity. Both this and the yield of the addition reaction are markedly dependent upon the temperature, as in the case of the ethyl ester.[156] The yield for the addition reaction depended upon the bromine concentration. The effect of change of wave-length (4360A, 5470A) is as follows: ethyl ester, ratio of yields at 4360 to 5470A, 1.9, methyl ester, 2.3. For the addition reaction, the corresponding values were 2.3 and 1.9. For free maleic acid, the ratio of the yields for the isomerization were 5 · 4 . 1, for ultraviolet, blue and green light.

In the system: maleic acid, sulfuric acid and bromine, at high concentrations of maleic acid, the transformation quantum yield is 430 at 21°C.[157] At lower concentrations of maleic acid, it is less, and becomes dependent on both the light intensity and the concentration of the maleic acid. The light reaction may, under these conditions, be initiated by the reduction of bromic acid, hypobromous acid and bromine. Reduction of bromine by ferrous sulfate gives a yield of 10,000 molecules of fumaric acid per atom of bromine formed. The yield is practically independent of the concentration of the reactants as long as the ferrous ion concentration is less than 10^{-5}, but at higher concentrations it becomes dependent on the ferrous ion concentration. These studies were undertaken to provide additional evidence that bromine atoms are responsible for the photosensitized conversion.[158]

The quantum yield of the addition of bromine to dimethyl fumarate is of the order of magnitude found by Wachholtz for the bromination of diethyl maleate or fumarate. It is not essentially different when aqueous solutions are used.

Mercuric bromide and mercurous nitrate and perchlorate are said also to sensitize the photochemical change of maleic to fumaric esters.

Stoermer and Robert[159] found the rearrangement of the amide of crotonic acid into that of isocrotonic acid to be easily effected by a Uviol lamp. By the aid of a Heraeus quartz lamp, they effected to some extent the conversion of the corresponding acid. Under the influence of ultraviolet light, it was also easily possible to secure the addition of the elements of water, methyl or ethyl alcohol to the double bond. Aniline and ammonia also add with the greatest ease at the double bond of α,β-unsaturated acids; crotonic acid and aniline give, together with a little of the anilides of crotonic and isocrotonic acids, chiefly $CH_3CH(NHC_6H_5)CH_2COOH$ and some of its anilide, while ammonia yields chiefly $CH_3CH(NH_2)CH_2COOH$ and iminodibutyric acid, with only very little of the amide of crotonic acid.

The separation of the two anilides is extraordinarily difficult and even on irradiating the pure stable anilide the amount of isoanilide obtained was not sufficient to permit of complete separation by careful fractional crystallization.

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[156] Eggert, J., Wachholtz, F., and Schmidt, R., *Z. Elektrochem.*, **33**, 542 (1927).

[157] Wachholtz, F., *Z. Elektrochem.*, **33**, 542, 545 (1927).

[158] See also *Oesterr. Chem. Ztg.*, **30**, 110 (1927); *Z. physik. Chem.*, **135**, 147 (1928); Schmidt, R., *Z. physik. Chem.*, **B1**, 205 (1928).

[159] Stoermer, R., and Robert, E., *Ber.*, **55B**, 1030 (1922); *Chem. Abs.*, **8**, 2880 (1914); **16**, 3631 (1922).

With the Heraeus lamp the maximum rearrangement (40 per cent) of the amide of crotonic acid in acetone is attained in about two days. For the rearrangement of crotonic acid, toluene proved the best solvent.

Acrylic acid similarly treated with aniline gives $C_6H_5NHCH_2CH_2CONHC_6H_5$ and the deliquescent hydrochloride, melting about 64°C., of $C_6H_5NHCH_2CH_2COOC_2H_5$, a light yellow oil. From crotonic acid and paratoluidine was obtained ethyl *β-p*-toluidineobutyrate.

The conversion of the α-methylated mesaconic acid into citraconic acid is very difficult. In solution in water or methyl alcohol, the solvent appears to combine with the acid.[160] Quantum yields of 0.18 at 0.01 molar and 0.22 at 0.005 molar were reported by Vaidya [161] for 3130A for the isomerization of citraconic acid.

The acrylic acid esters prepared from glycerine, lactic acid, etc. when exposed to sunlight or ultraviolet light polymerize to varnish-like elastic masses. They are soluble in solvents for oils and are said to dry rapidly and not to be readily affected by exposure or by chemical agents.[162]

Malachowski and Maslowski [163] have prepared the α-, β-, and γ-*trans*-monomethyl esters of aconitic acid by irradiating the *cis* compounds in the presence of bromine by direct sunlight or a mercury arc.

Little, if any, work has been done on the photochemistry of the higher saturated fatty acids, but the long-chained unsaturated fatty acids have been frequently studied. The results of this work are discussed in Chapter 30 in connection with the behavior of drying oils.

Compounds Containing Nitrogen

Cyanogen Compounds. Hydrogen cyanide has no absorption spectrum between 2800A and 2100A but possesses a series of bands between 2001 and 1789A.[164] A few observations on the decomposition of hydrogen cyanide in cherry-laurel water have been reported by Andant and Rousseau.[165] They believed, since they found about as much (slight) decomposition to be effected by the 3650A line as by the total radiation of an arc to 3130A, that ultraviolet effects are nullified by the longer wave-lengths. They state that 0.126 gm. of manganese chloride in cherry-laurel water increases the action of ultraviolet rays so that the loss of hydrocyanic acid reaches 10.1 per cent in the first thirty minutes of irradiation and 30.0 per cent after two hours. They were inclined to attribute the activity to visible light.

Cyanogen is transformed into paracyanogen by ultraviolet rays.[166] On exposure to sunlight, cyanogen slowly polymerizes. In the presence of oxygen and ultraviolet light, it is oxidized completely to carbon dioxide and nitrogen. Hogness and Tsai,[167] observed in cyanogen gas at one atmosphere a series of diffuse bands beginning at 2240A and extending to the limits of dispersion of the quartz of their spectrograph. Their diffuse nature indicated the primary process to be one of predissociation, the available evidence indicating the products to be two CN molecules, one of which is excited.[168] The quantum efficiency for the polymerization by a hydrogen discharge source was found to be three. These authors were unable to confirm the observations of Berthelot and Gaudechon with the mercury arc, since cyanogen does not absorb any mercury lines.

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[160] Stoermer, R., *Ber.*, **44**, 637 (1911).

[161] Vaidya, B. K., *Proc. Roy. Soc.*, **A129**, 299 (1930).

[162] Morrell, R. S., and de Waelle, A., "Rubber, Resins, Paints and Varnishes," New York, D. Van Nostrand Company, Inc., 1921.

[163] Malachowski, R., and Maslowski, M., *Ber.*, **61B**, 2521 (1928).

[164] Villars, D. S., *J. Am. Chem. Soc.*, **52**, 61 (1930); Hilgendorf, H. J., *Z. Physik*, **95**, 781 (1935).

[165] Andant, A., and Rousseau, E., *Compt. rend.*, **184**, 683, 1553 (1927); *Compt. rend. soc. biol.*, **96**, 613 (1927); *Chem. Abs.*, **21**, 3161 (1927).

[166] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1169 (1910); *J. Chem. Soc.*, **98**, ii, 349 (1910).

[167] Hogness, T. R., and Tsai, L. S., *J. Am. Chem. Soc.*, **54**, 123 (1932).

Norrish and Smith[169] have described two reactions occurring when a mixture of nitric oxide and cyanogen is illuminated by radiations between 3600 and 2200A.

$$4NO \longrightarrow N_2 + 2NO_2.$$
$$4NO + (CN)_2 \longrightarrow 3N_2 + 2CO_2.$$

In the first of these, which occurs six times as extensively as the second, the cyanogen plays the part of a catalyst. Neither reaction occurs in the absence of a small amount of oxygen, which accumulates as the reaction proceeds, the effect being autocatalytic. The previously unknown molecule, NOCN, was suggested as an intermediary product.

A carbon tetrachloride solution of thiocyanogen $(SCN)_2$, according to Kaufmann and Liepe,[170] polymerizes readily in the sunlight. In ethereal solutions, substances having powerful odors are formed. Soderbäck[171] finds the addition of thiocyanogen to ethylenic hydrocarbons, which is very slow at ordinary temperatures, to go smoothly when the reactants are exposed in dry benzene solution to the action of actinic rays, yielding dithiocyanoethanes of the type CNS.CHR.CHR.CNS. Only two thiocyanogen radicals will combine with acetylenic hydrocarbons, giving compounds of the type $CR'(CNS)=CR''CNS$. Aromatic acetylene derivatives combine readily at the ordinary temperature in the dark, but aliphatic acetylenes require intense photocatalysis to cause addition. Interconversion of *cis* and *trans* forms under the influence of ultraviolet light occurs with the compounds obtained from acetylenes, a 0.02*N* solution of free thiocyanogen in benzene being an effective catalyst for the change. Acetylene itself yields a solid *s*-dithiocyanoethylene, melting 97-98.5°, and a liquid form, melting 15-17°, which are interconvertible under the influence of light.

Irradiation of fumaronitrile in acetone with ultraviolet light for 100 hours gives maleonitrile and an additive compound.[172]

Ganassini[173] finds that sunlight produces a yellow color in allylisothiocyanate and that, after a month, it deposits a precipitate. In the presence of water, decomposition occurs to the extent of 5 per cent and, in its absence, to the extent of 15 per cent, air being present in either case. He suggested the following possible reactions.

$$3C_3H_5NCS + 3H_2O \longrightarrow C_3H_5NH_2 + (C_3H_5)_2O + 2HCNS + H_2S + CO_2$$
$$9HCNS \longrightarrow 2(CNS)_3 + 3HCN + 3H_2S.$$

Sulfuric acid and ammonia are also formed by secondary reactions.

The polymerization of methylacrylonitrile in ultraviolet light has been described by Mertens and Fonteyn.[174] Considerable information has been obtained regarding the absorption spectra of the nitriles and amides of many acids.[175]

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[168] See also Mooney, R. B., and Reid, H. G., *Nature,* **128,** 271 (1931).

[169] Norrish, R. G. W., and Smith, F. F. P., *Trans. Faraday Soc.,* **24,** 620 (1928)

[170] Kaufmann, H. P., and Liepe, J., *Ber.,* **56B,** 2514 (1923)

[171] Söderbäck, E., *Annalen,* **443,** 142 (1925).

[172] Jennen, J., *Bull. soc. chim. Belg.,* **46,** 258 (1937); *Brit. Chem. Abs.,* **A** II, 404 (1937), *Chem. Abs.,* **32,** 500 (1932).

[173] Ganassini, D., *Arch. ist. biochim. ital.,* **3,** 1 (1931); *Chem. Abs.,* **26,** 2657 (1932).

Amines. Dissolved in hexane, ammonia has a band at about 1920A, which is displaced toward shorter wave-lengths in aqueous solution.[176] Other amines exhibit similar solvent effects.

In the gaseous state, the amines exhibit a series of diffuse predissociation absorption bands, increasing in intensity toward the shorter wave-lengths, and attributed to an electronic excitation in the amino- group.[177] In methylamine the predissociation bands begin at 2440A and in ethylamine at 2370A.[178]

Berthelot and Gaudechon [179] found ethyl- and methylamine, guanidine, and hydroxylamine, when subjected to ultraviolet radiations, to be converted first into ammonia and then into nitrites. Emeléus and Jolley state that methylamine, on exposure to light from a mercury arc or an aluminum spark, produces equal amounts of ammonia and hydrogen and a liquid, with small quantities of methane and nitrogen. Ethylamine gives the same gaseous products and small quantities of ethane and ethylene. Benzene has also been found among the products.[180] Decomposition quantum yields of about 0.75 are found. The primary reaction is believed to form CH_3NH and H, rather than CH_3 and NH_2.[181] The photoöxidation of methylamine yields principally ammonia; the quantum yield is again 0.75.

In the presence of zinc oxide, or titanium dioxide, the aliphatic amines are oxidized to nitrites in sunlight more readily than are the aromatic amino- derivatives. The amines are first hydrolyzed and then the ammonia is oxidized to nitrite and the alcohol to an aldehyde.[182]

Amides. Berthelot and Gaudechon [183] state that equal volumes of carbon monoxide and ammonia combine in a few hours to give formamide under the influence of rays of wave-length about 2000A to 3000A. Formamide also slowly decomposes when submitted to ultraviolet rays, the reaction being complicated by dehydration and formation of hydrogen cyanide. Light, less markedly than heat, produces polymerization.[184] The titanium dioxide-sensitized decomposition in sunlight proceeds more rapidly in the amides of monobasic than in those of dibasic acids.[185]

On exposure to ultraviolet rays [186] urea is said to be converted first into ammonia and then into a nitrite. Kailan,[187] however, found that a normal solution of urea irradiated for 48 hours by a quartz mercury lamp (or for 1632 hours with the rays from 80 mg. of radium) showed no change in density, refractive index, or rate of change into ammonium cyanate, other than could be accounted for by experimental error.

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[174] Mertens, E., and Fonteyn, M., *Bull. soc. chim. Belg*, **45**, 438 (1936); *Chem Abs.*, **30**, 8152 (1936)

[175] Bruylants, P., and Castille, A., *Bull. soc. chim. Belg.*, **34**, 261 (1925); Castille, A., and Gueuden, J., *Ann. soc. scient. Bruxelles*, **47B**, 56 (1927); Castille, A., and Ruppol, E., *Bull. sci. acad roy Belg.*, **16**, 1129 (1930); *Bull. soc. chim. Belg.*, **40**, 243 (1931); **44**, 351 (1935); Castille, A., *Bull. sci acad. roy. Belg.*, **16**, 811 (1930); Ruppol, E., *Bull. sci. acad. roy. Belg*, **21**, 236 (1935); Herzberg, G., and Scheibe, G., *Trans. Faraday Soc.*, **25**, 716 (1929).

[176] Ley, H., and Arends, B., *Z. physik. Chem.*, **B17**, 177 (1932); for the absorption of alkyl amines, see Ramart-Lucas, Mme., *Compt. rend.*, **194**, 726 (1932); Grunfeld, M., *Ibid*, **194**, 1083 (1932).

[177] Herzberg, G., and Kölsch, R., *Z. Elektrochem.*, **39**, 572 (1933). Analyses of the methylamine bands have been given by Henri, V., and Lasareff, W., *Compt. rend.*, **200**, 829 (1935), *J. chim phys.*, **32**, 353 (1935).

[178] Emeléus, H. J., and Jolley, L. J., *J. Chem. Soc.*, 1612 (**1935**).

[179] Berthelot, D., and Gaudechon, H, *Compt. rend.*, **152**, 522 (1911).

[180] Emeléus, H. J., and Taylor, H. S., *J. Am. Chem. Soc.*, **53**, 2370 (1931).

[181] Emeléus, H. J., and Jolley, L. J., *loc. cit.*

[182] Rao, G. G., and Pandalai, K. M., *J. Indian Chem. Soc.*, **11**, 623 (1934); *Brit. Chem. Abs.*, **A** 1316 (1934).

[183] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **155**, 207 (1912).

[184] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **150**, 1164 (1910); **151**, 478 (1910).

[185] Rao, G G., and Pandalai, K. M., *J. Indian Chem. Soc.*, **11**, 623 (1934); *Chem. Abs*, **29**, 1326 (1935).

[186] Berthelot, D., and Gaudechon, H., *Compt. rend*, **152**, 522 (1911).

[187] Kailan, A., *Z. physik. Chem.*, **95**, 215 (1920); *J. Chem. Soc.*, **118** (ii), 576 (1920).

Azomethane. This compound begins to absorb at about 4000A, exhibits a maximum at 3390A, a minimum at 2700A and increasing absorption at shorter wave-lengths. No evidence of definite bands appears.[188]

Ramsperger followed the photodecomposition by pressure measurements from which he concluded the reaction to be mainly

$$CH_3NNCH_3 \longrightarrow N_2 + C_2H_6.$$

He found the temperature coefficient to be about zero and the quantum yield two, the latter remaining practically constant over a two hundred-fold pressure range. To explain this result, Ramsperger made the assumption that the ethane molecule bore enough energy, derived from the heat of reaction and from the excess energy of the 3660A line employed over the energy required for the photodecomposition, to effect the decomposition of a second molecule of azomethane on collision with it. This theory would, however, be difficult to reconcile with the independence of the quantum yield and the pressure.

Since Ramsperger had used the "treacherous method of filters" in his quantum yield determinations, Forbes, Heidt and Sickman[189] repeated them, using for the energy determinations the uranyl oxalate actinometer. They made determinations at six wave-lengths of monochromatic light and at various pressures. At low pressures they found the quantum yield to approach unity as its upper limit, at least for the initial decomposition. It decreases with increasing decomposition at room temperature and also with increasing pressures. The latter points to a collisional deactivation. It was necessary in the measurements to use a graphical method of correcting for errors due to the deposition of difficultly volatile decomposition products upon the window. The quantum yields passed through a maximum in the region 3660 to 3350A, corresponding to the maximum of absorption by the N—N bond. At shorter wave-lengths they decreased, but began to increase again when wave-lengths absorbed by the N—C bond were employed. In agreement with Ramsperger, the temperature coefficient was zero at temperatures below 260°C.

That the decomposition is not a chain reaction between 20° and 226°C. was confirmed by Patat,[190] who believed the primary reaction to yield nitrogen and two methyl groups. His evidence for this was the fact that dimethyl ether at 150 to 600 mm. pressure could be decomposed in the presence of 10 to 30 mm. of irradiated azomethane. That the free methyl radicals did not form chains indicated the activation energy for the reaction between methyl and azomethane to be greater than 20 kcal. Burton, Davis and Taylor[191] believe quantum yield determinations based only on the pressure increase are too low. They find the amount of nitrogen produced in experiments at various temperatures always exceeds that of the hydrocarbons. The excess is a maximum at about 200°C. Methane increases and ethane decreases at the higher temperatures. The amount of higher hydrocarbons increases with the degree of decomposition and with lowering of temperature. No hydrogen and only a little unsaturated hydrocarbon are produced. Burton, Davis and Taylor doubt that the temperature coefficient is zero below 226°C. They suggest the occurrence of a secondary association reaction between methyl radicals and $(CH_3N)_2$. When nitric oxide is present during photolysis, practically no alkane gas is produced.[192] From analyses of the reaction under these conditions, it is concluded that the source of ethane and other alkanes in the ordinary photolysis is not the combination of free radicals, but the decomposition of the association product with azomethane.

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[188] Ramsperger, H. C., *J. Am. Chem. Soc.*, **50**, 123 (1928); for observations on azoisopropane, see *Proc. Nat. Acad. Sci.*, **13**, 849 (1927).

[189] Forbes, G. S., Heidt, L. J., and Sickman, D. V., *J. Am. Chem. Soc.*, **57**, 1935 (1935); see also Heidt, L. J., and Forbes, G. S., *Ibid.*, 2331.

[190] Patat, F., *Naturwiss.*, **23**, 801 (1935); *Nachr. ges. Wiss. Göttingen, Math.-physik. Klasse, Fachgruppe II*, [*N.F.*], **2**, 77 (1936); *Chem. Abs.*, **31**, 6112 (1937).

[191] Burton, M., Davis, T. W., and Taylor, H. A , *J. Am. Chem. Soc.*, **59**, 1038, 1989 (1937).

Diazo-Compounds. Diazomethane exhibits an absorption spectrum somewhat resembling that of azomethane.[193] It consists of a series of weak diffuse bands in the region 4710 to 4250A, followed by a continuum from 4250 to 3200A, and a second completely continuous region beginning at 2650A. The photochemical decomposition is unimolecular; the main products are nitrogen, ethylene, ethane and a non-volatile liquid. The quantum yield is approximately four at 3650 and 4360A. The primary process is the decomposition: $CH_2N_2 + h\nu \rightarrow CH_2 + N_2$. This is supported by the behavior of mixtures of the gas with hydrogen and with oxygen.

Adamson and Kenner[194] find that vinyldiazomethane, $CH_2{=}CHCH{=}N_2$, in 0.5-per cent ether solution forms pyrazole by a monomolecular photochemical reaction.

Ethyl diazoacetate, as such or in various solvents,[195] has an absorption curve similar to that of compounds containing a carbonyl group since both chromophores N=N and CO are said to have the same electron-term scheme. In the photolysis in heptane solution, the quantum yield rises from 0.20 for 4200A to 1.11 for 2600A; the rate of increase is small at first, but becomes greater in the band of shorter wave-length. In ethanol, methanol and water, there is a similar rise, but compared with heptane the values are smaller in the longer ultraviolet and greater in the shorter. For a given wave-length, the quantum yield either rises or falls in the order: heptane, ethanol, methanol, water. Neither a ten-fold increase in concentration nor a rise in temperature from 5° to 40°C. affects the quantum yield.

Goldfinger[196] measured manometrically photodecomposition by the full radiation of the mercury arc at various initial pressures from 0.04 to 297 mm. The relative velocity is greatest for the lowest pressure; the order of the reaction lies between zero and two. At low pressures, it is accelerated by argon. At higher pressures, it is retarded by nitrogen and by methane.

Nitro- Compounds. Chloropicrin is decomposed by violet or ultraviolet light, but the reaction soon stops because the nitrosyl chloride formed acts as an internal filter.

$$Cl_3CNO_2 + h\nu \longrightarrow NOCl + COCl_2.^{197}$$

According to Thompson and Purkis[198] methyl nitrite yields on photolysis a solid containing paraformaldehyde and formic acid, with small amounts of carbon monoxide and hydrogen, and 45 per cent each of nitrogen and nitrous oxide. In the case of ethyl nitrite, the volume decrease is less and the fraction of noncondensible gases is larger. Aldehydes are present in a liquid residue. The residual gas has 38 per cent of nitrogen, 30 per cent of nitrous oxide, 18 per cent of carbon monoxide and 13 per cent of methane.

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[192] Davis, T. W., Jahn, F. P., and Burton, M., *J. Am. Chem. Soc.*, **60**, 10 (1938).

[193] Kirkbride, F. W., and Norrish, R. G. W., *J. Chem. Soc.*, 119 (1933).

[194] Adamson, D. W., and Kenner, J., *J. Chem. Soc.*, 286 (1935).

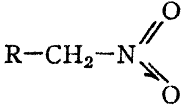
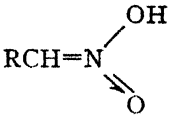
[195] Wolf, E., *Z. physik. Chem.*, **B17**, 46 (1932).

[196] Goldfinger, G., *Compt. rend.*, **202**, 1502 (1936).

[197] Radulescu, D., and Zamfirescu, G., *Bul. soc. chim. Romania*, **17**, 87 (1935); *Chem. Abs.*, **30**, 671; see also Piutti, A., *Atti I Congr. naz. Chim. pura applicata*, 437 (1923); *J. Chem. Soc.*, **120**, 298 (1921); Piutti, A., and Mazza, F. P., *Gaz. chim. ital.*, **57**, 610 (1927); Alekseevskiĭ, E. V., *J. gen. Chem. (U.S.S.R.)*, **2**, 341 (1932).

In the wave-length range 2000 to 3000A, the primary process is believed[199] to be in the case of nitro-compounds

$$RCH_2NO_2 + h\nu \longrightarrow RCHO + NOH$$

This is followed by certain reactions of NOH and by oxidation of the aldehyde. It is assumed that light absorbed by the molecule  $R-CH_2-N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$ changes it to the form  $RCH{=}N\begin{smallmatrix}\nearrow OH\\ \searrow O\end{smallmatrix}$, and that this is followed by a rupture of the molecule.

In the photolysis of tetramethylene nitrosochloride, the primary process, according to Hammick and Lister[200] is the elimination of NOH, the resulting olefin undergoing further reactions. The quantum yield is approximately unity. If the carbon atom to which the NO group is attached is also linked to an atom other than carbon, a photoöxidation occurs in the presence of oxygen with unit quantum efficiency. In the absence of oxygen, 1-chloro-1-nitroso-cyclohexane undergoes a rapid photoreaction without the evolution of gas. Red light decomposes nitroso-isopropylacetone to $H_2N_2O_2$ and its decomposition products and mesityl oxide. β-nitroso-β,ϵ-dimethylhexane probably gives a β,ϵ-dimethylhexene.[201]

Milone[202] finds ultraviolet irradiation to isomerize the α- and γ-forms of certain glyoximes, both in the solid state and in dilute alcohol, at 18°C., to the β-forms. The isomerization is also promoted very slowly by sunlight, but Wood light (3650A) is ineffective. Isomerization is more rapid in 30-40-per cent ethyl alcohol than in the solid state, as shown by the following data, which give the hours of exposure and the percentage of β-compound formed in solution and in the solid state, respectively: α-phenylglyoxime, 23,44.8; 17,20.7; α-p-tolylglyoxime, 22,28.8; 19,20.2; α-methylphenylglyoxime, 21,30.3; 19,15; α-diphenylglyoxime, 26,29; 20,15.9; γ-diphenylglyoxime, 28,41; 19,22.4. In sunlight, behind glass, γ-phenylglyoxime yielded only 0.93 per cent of the β-compound after 16 months.

After thirty minutes of exposure to ultraviolet rays, 0.10 gm. of nitroglycerin at 20 mm. gave 1.32 cc. of gas containing carbon dioxide, 24 per cent, carbon monoxide, 10.5 per cent, nitrogen, 17.5 per cent, nitrous oxide, 8.5 per cent and nitric oxide 39.5 per cent.[203] Some nitric oxide was destroyed in attacking the mercury in the testing apparatus. The high percentage of nitric oxide explains

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[198] Thompson, H. W., and Purkis, C. H., *Trans. Faraday Soc.*, **32**, 674, 1466 (1936); for absorption data on nitrites and nitro-compounds, see also Goodeve, C. F., *Trans. Faraday Soc.*, **30**, 504 (1934); Kuhn, W., and Lehmann, H. L., *Z. physik. Chem.*, **18B**, 32 (1932)

[199] Hirschlaff, E. N., and Norrish, R. G. W., *J. Chem. Soc.*, 1580 (1936), see also Thompson, H. W., and Dainton, F. S., *Trans. Faraday Soc.*, **33**, 1546 (1937), for the decomposition of alkyl nitrites.

[200] Hammick, D. L., and Lister, M. W., *J. Chem. Soc.*, 489 (1937).

[201] Anderson, K. D., Crumpler, C. J., and Hammick, D. L., *J. Chem. Soc.*, 1679 (1935).

[202] Milone, M., *Gazz. chim. ital.*, **63**, 744 (1933); *Chem. Abs.*, **28**, 2713 (1934).

[203] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **154**, 201 (1912).

its presence in the products of decomposition of smokeless powders containing nitroglycerin.

Berthelot and Gaudechon[204] made this behavior the basis of a test for the stability of smokeless explosives. Samples were cut into cylinders weighing 0.25 to 0.45 g., placed over mercury in a quartz tube, containing nitrogen or carbon dioxide, and exposed to the radiations from a quartz mercury lamp at a distance of 78 to 80 mm. for six hours. Powders consisting only of nitrated cellulose were thought to be more stable than those containing nitroglycerin. An English Cordite containing 30 per cent of the latter and 5 per cent of Vaseline, exposed in one cubic centimeter of carbon dioxide, gave a mixture composed of the following volumes of gases: CO_2, 1 cc.; CO, 0.17 cc.; NO, 0.10 cc.; N_2O, 0.02 cc.; N_2, 0.10 cc. Results were also given for the French A and B powders and for Balistite of different ages and with stabilizers.

Experiments were also made in oxidizing (oxygen), reducing (hydrogen) and inert (carbon dioxide, nitrogen) atmospheres.[205] With oxygen, two-thirds of the free oxygen disappeared and added its oxidizing effect to that of the oxygen of the nitrocellulose. With hydrogen, about one-quarter disappeared, forming water and formaldehyde. With carbon dioxide, much depended on the temperature. At 25° to 30°C. (70 to 80 mm. from the lamp) there was absorption, due no doubt to the solvents and stabilizers which are basic in their character; at 40°C. (50 mm. distance) no change in volume occurred; at 75°C. (20 mm. distance) there was disengagement of carbon dioxide from the powder and the final volume showed an increase. Nitrogen had no effect on the evolution of nitrogen or nitrous gases from the powder.

Comparison[206] of two powders of the same age and make and stabilized by amyl alcohol and diphenylamine, respectively, showed that at 20 mm. (75°C.) amyl alcohol is the more efficient, the latter powder giving off less gas, and the gas containing a very much lower percentage of nitric oxide than the former. At 50 mm. (40°C.), on the other hand, diphenylamine is the more efficient stabilizer. Similar results were obtained with two naval powders, save that these evolved no nitrogen oxides. When the powders were treated with alkali (one gram with 20 cc. of 0.5*N* potassium hydroxide for 30 minutes at 15°C.), it was found that the diphenylamine powder showed less decomposition than that stabilized with amyl alcohol. A damaged naval powder, in which the brownish-yellow plates showed whitish stripes, was examined by the lamp. At both distances, the damaged part gave off more gas than the unaltered part, and this gas contained from 12 to 30 per cent of nitrogen oxide, while the gas from the unaltered part contained none.

A piece of nitrocellulose (collodion) 15 by 51.6 mm., after two hours at 20 mm., gave 0.87 cc. of gas, the percentages of its constituents being CO_2 25.5, CO 10.5, NO 39, N_2O 7, N_2 9.[207] Collodion, though less heavily nitrated than the French service smokeless powders, decomposed more readily and evolved a notable amount of nitric oxide.

Holmes and Patrick[208] stated that celluloid, when exposed to ultraviolet light, becomes brown and brittle with liberation of gaseous products, and that it not only absorbed liquid but the gel itself is decomposed by the rays. More recently, however, Clément, Rivière and Beck[209] state that ultraviolet light does not exert a destructive effect on celluloids, or nitrocelluloses; instead, it seems to effect a molecular polarization which renders them difficult of esterification. Nitrocellulose, loose or in the form of collodion, decreases considerably in viscosity and the alcohol solubility increases. This is true, however, of only high-viscosity nitrocellulose. Samples with very low viscosities are unaffected by ultraviolet light. Traces of phenolic compounds produce intense yellow coloration with nitrocellulose products exposed to ultraviolet. The viscosity of acetone-soluble nitrocellulose also decreases on exposure but the degree of acetylation is unaffected. Films of cellulose acetate containing phenolic compounds become colored when irradiated. The irradiation of benzyl cellulose, in powder form, results in the formation of a high content of insoluble matter; irradiation of a benzyl cellulose solution does not decrease its viscosity. Other celluloses remain stable when irradiated; the viscosity of ethyl cellulose Celloidin is considerably reduced by irradiation. (See further Chapter 30.)

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[204] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **153**, 1220 (1911).

[205] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **154**, 514 (1912).

[206] Berthelot, D., and Gaudechon, H., *Compt. rend*, **154**, 201 (1912).

[207] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **154**, 201 (1912).

[208] Holmes, E. O., Jr., and Patrick, W. A., *J. Phys. Chem.*, **26**, 25 (1922).

Long exposure of mercury fulminate, $Hg(ONC)_2$, to ultraviolet converts it to a black, more flammable but less explosive compound of equal mercury content.[210]

SULFUR COMPOUNDS

Carbon disulfide in admixture with argon undergoes a partial decomposition when exposed to bright sunlight and the sides of the containing vessel become coated with a brown deposit;[211] when exposed to diffused light, it remains unaltered. Bruhat and Pauthenier[212] have observed the decomposition of carbon disulfide by ultraviolet rays. When this substance is exposed in quartz cells to the quartz mercury arc, a deposit of sulfur is formed on the walls. In order to fix the sulfur, the interior of the cells was coated with a thin film of silver, which is transparent to the ultraviolet. For a six-hour exposure, the long wave-length limit of decomposition was found to be at 3660A.

Light catalyzes a reaction of mercaptan in contact with copper and with mercury in the presence of air.[213] When aqueous neutral solutions or alkaline solutions of sodium hydrosulphide, ethyl mercaptan, thioglycollic acid, cysteine, etc., are exposed to the radiation of a strong mercury arc, hydrogen is produced with the simultaneous formation of the corresponding disulfide compound. The quantum efficiency with respect to hydrogen formation is always much less than one, indicating that reverse reactions occur. The primary process is probably a decomposition into RS and H. In aqueous solution, where a certain amount of the anion RS′ is present the process may be $RS'(HOH)+h\nu \rightarrow RS+H+OH'$. This is followed by the formation of hydrogen from hydrogen atoms and of RSSR from two RS. A splitting of the RSH compound into RH and S may also occur as the primary process.

Many sulfhydryl compounds react with fluorescent dyestuffs in the dark. Irradiation with light absorbed by the dyestuff accelerates this reaction.[214]

Rathke[215] showed that the photopolymerization product of thiophosgene is a dimer. Schönberg and Stephenson[216] confirm this, but believe it to be 2,2,4,4-tetrachloro-1,3-dithiacyclobutane, $\mathrm{Cl_2\,C} \overset{\mathrm{S}}{\underset{\mathrm{C}}{<\;>}} \mathrm{C\,Cl_2}$ rather than $ClCS_2CCl_3$, and that its condensation product with aniline is 4,4-dichlor-1,3-dithiacyclobutane-2-one anil. It turns brown when illuminated a short time and is depolymerized to thiophosgene in petroleum ether by the light of a quartz lamp.

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[209] Clément. L., Rivière, C., and Beck, A , *Chimie et industrie*, Special No. 702 (March, 1932); *Chem. Abs.*, **26**, 3662 (1932).

[210] Patry, M., and Laffitte, P., *Bull. soc. chim* , **51**, 1205 (1932).

[211] Berthelot, D., *Ann. Chim. Phys.*, **19**, 150 (1900).

[212] Bruhat, G., and Pauthenier, M., *Compt. rend.*, **178**, 1536 (1924).

[213] Dittrich, E., *Brennstoff-Chem* , **15**, 148 1934); *Chem. Abs.*, **28**, 5806 (1934).

[214] Weiss, J., and Fishgold. H., *Nature*, **137**, 71 (1936).

[215] Rathke, B., *Ber.*, **21**, 2539 (1888).

Lifschitz and Froentjes[217] prepare the β-form of ethyl-α-thiolactic acid platinum, $Pt(CH_3CHSC_2H_5COO)_2$, from the α-form by exposure to the quartz mercury lamp, or better by exposure in aqueous solution to direct sunlight.

ORGANOMETALLIC COMPOUNDS

Lead tetramethyl and tetraphenyl decompose in ultraviolet light, which is absorbed continuously, into metallic lead and hydrocarbons. The former yields methyl radicals. For the vapor phase reaction, the quantum yield is 1.11, but in trimethylpentane, it is about 0.39, as determined by a method employing radioactive indicators. In the vapor phase reaction, oxygen breaks the chains.[218] The absorption spectrum of dimethyl zinc shows a continuum at approximately 2400A, that of diethyl zinc shows diffuse bands with an overlapping continuum at approximately 2400A, and lead tetraethyl shows a quite sharp band in the region between 2300 and 2700A.[219]

Mercury dimethyl, irradiated by the 2537A line, yields mercury, methane and ethane with a quantum yield of unity. Ethane constitutes 93 per cent of the hydrocarbons.[220] Methane is formed in amounts increasing at increasing temperatures. The primary process may yield mercury and ethane directly, although subsidiary processes may give free methyl radicals. At 462°K the quantum yield rises to 2.21, chains being involved. At room temperature in the presence of nitric oxide, a white solid is formed, but the quantum yield for the disappearance of mercury dimethyl is still unity. Aerosols[221] have been prepared by the photochemical decomposition of mercury dimethyl.

Space does not permit the discussion of the interesting chemiluminescence of the Grignard compounds, nor of their photovoltaic effects.[222]

Little work has been reported on the effects of irradiating such compounds. Gilman and Heck[223] note that although either heat or ultraviolet irradiation transforms isobutyl bromide to tertiary butyl bromide reversibly, irradiation produces no effect on isobutyl magnesium bromide or tertiary butylmagnesium chloride.

Müller, Frankenburger and Grassner[224] remove metal carbonyls from synthetic methanol or other liquids containing less than 10 per cent of iron or other metal carbonyl by exposure to ultraviolet rays, which also act on any aldehydes or ketones present. According to Reihlen, Gruhl and von Hessling[225] irradiation of a mixture of ethyl mercaptan and an excess of iron pentacarbonyl greatly accelerates the reaction by which are formed hydrogen, carbon monoxide and *bis*-ironmercaptotricarbonyl:

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[216] Schönberg, A , and Stephenson, A., *Ber.*, **66B**, 567 (1933).

[217] Lifschitz, I., and Froentjes, W., *Z. anorg. Chem.*, **224**, 173 (1935).

[218] Leighton, P. A., and Mortensen, R. A , *J. Am. Chem. Soc.*, **58**, 448 (1936).

[219] Thompson, H. W., *J. Chem. Soc.*, 790 (1934); *Proc. Roy Soc.*, **150A**, 603 (1934); see also Thompson, H. W., and Frewing, J. J., *Nature*, **135**, 507 (1935).

[220] Linnett, J. W., and Thompson, H. W., *Trans. Faraday Soc.*, **33**, 501, 874 (1937); see also Prileshaeva, N , and Terenin, A., *Ibid.*, **31**, 1483 (1935); *Acta Physicochim U.R.S S*, **1**, 759 (1934); *Chem. Abs.*, **29**, 7798 (1935); Cunningham, J. P., and Taylor, H. S , *J. Chem. Phys.*, **6**, 359 (1938).

[221] Harms, J., and Jander, G., *Kolloid-Z.*, **77**, 267 (1936).

[222] Dufford, R. T., *J. Phys. Chem.*, **35**, 988 (1931); **37**, 709 (1933).

[223] Gilman, H., and Heck, L. L., *Bull. soc. chim.*, **45**, 1095 (1929).

[224] Müller, C., Frankenburger, W., and Grassner, F., U. S. P. 1,679,256, July 31, 1928, to I. G Farbenind. A.-G.; *Chem. Abs.*, **28**, 3669 (1928)

[225] Reihlen, H., Gruhl, A., and von Hessling, G., Annalen, **472**, 268 (1929); *Brit. Chem. Abs.*, **1929A**, 1050.

$$2Fe(CO)_5 + 2C_2H_5SH \longrightarrow 4CO + H_2 + Fe_2(SC_2H_5)_2(C_3O_3)_2$$

A secondary reaction also occurs in which there is probably a slow decomposition of the *bis*-ironmercaptotricarbonyl to iron mercaptide.

With a mixture of equal volumes of the reactants at 3° to 5°C., the ratio of hydrogen to carbon monoxide evolved is 1:9.2. This is due to the reaction yielding instead of 4 molecules of carbon monoxide and one of hydrogen, three of carbon monoxide and one of formaldehyde, which is polymerized during the irradiation. In both of these cases, the primary reaction seems to be the loss of one molecule of carbon monoxide from two molecules of iron pentacarbonyl with the formation of $Fe_2(CO)_9$, which then reacts with two molecules of the mercaptan to yield the *bis*-ironmercaptotricarbonyl and $H_2C_8O_3$. This latter product then breaks down to yield three molecules of carbon monoxide and one of hydrogen at the higher temperatures, or two molecules of carbon monoxide and formaldehyde at low temperatures.

When a mixture of one volume of iron pentacarbonyl and five of acetylacetone is irradiated at about 30° until evolution of gas ceases, the products formed are hydrogen, carbon monoxide, ferric acetylacetone and a substance which is probably an impure peroxide of ferrous acetylacetone. From 20 to 25 per cent of the carbonyl is unchanged. Nickel carbonyl and acetyl chloride react at 50° to 55°C., but the reaction is not affected by irradiation.

The decomposition of iron pentacarbonyl in toluene and alcohol may be sensitized by pinacyanol to wave-lengths longer than 6400A.[226]

[226] Fedorov, F. P., and Talmud, D. L., *J. Phys. Chem. (U.S.S.R.)*, **8**, 789 (1936); *Chem. Abs.*, **31**, 1702 (1937).

Chapter 25

Aromatic Compounds

Berthelot and Gaudechon[1] called attention to the stability of a number of typical aromatic compounds toward ultraviolet radiations. This is in general agreement with the stability of the aromatic nucleus toward heat and chemical reagents. A similar stability has also been noted in other cyclic compounds, such as pyrrole, furfural, pyridine and a few alkaloids. In substituents which may be present, however, may occur any of the types of photochemical change encountered in these substances when unattached to the benzene ring. When the double linkings in the ring have been saturated, as in hexahydrobenzene and piperidine, ultraviolet irradiation may cause decomposition. Cyclopropane, which does not absorb wave-lengths longer than 2000A, undergoes a mercury-sensitized photopolymerization under the influence of the 2537A line to a colorless oil of high boiling point.[2]

HYDROCARBONS

Berthelot[3] found that benzene remains unaltered when exposed to bright sunlight for several months in sealed tubes containing hydrogen or argon, although it combined with oxygen, yielding resinous products, if placed over mercury. A brown sediment, derived from the thiophene present in the benzene, formed at the junction of the liquids.[4]

Benzene vapor exhibits a complex absorption spectrum, analyses of which have been given by Henri.[5] The absorption of light produces only excited states, and most is reëmitted as fluorescence. From the fluorescence spectrum, Almasy[6] has drawn certain conclusions as to a predissociation of the molecule. Actually, however, little decomposition can be effected below about 600°C. by irradiation. With increasing temperatures, the fine structure of at least four of the bands of the benzene vapor spectrum successively disappears, and underlying continuous absorption increases. Henri and Cartwright suggested that incompletely separated molecules of C_8H_8 are formed by an excessive folding of the benzene ring, but that these recombine on cooling. This was proposed in an attempt to account for the predissociation spectra observed at higher temperatures.

In hexane, benzene exhibits a series of about seven relatively broad bands.[7] Kwieninski and Marchlewski[8] locate the maxima of six bands at 2648, 2608, 2546,

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[1] Berthelot, D., and Gaudechon, H., *Compt. rend.*, **152**, 376 (1911).

[2] Harris, L., Ashdown, A. A., and Armstrong, R. T., *J. Am. Chem. Soc.*, **58**, 852 (1936).

[3] Berthelot, D., *Ann. Chim. Phys.*, **19**, 150 (1900).

[4] *J. Soc. Chem. Ind.*, **47**, 727 (1928); *Report of Joint Research Committee of the National Benzol Association, and the University of Leeds*, 237 (1928).

[5] Henri, V., *J. phys. Radium*, **3**, 181 (1922); Henri, V., and Cartwright, C. H., *Compt. rend.*, **200**, 1532 (1935); Kistiakowsky, G. B., and Solomon, A. K., *J. Chem. Phys.*, **5**, 609 (1937).

[6] Almasy, F., *Naturwiss.*, **20**, 296 (1932); Almasy, F., and Shapiro, C. V., *Z. physik. Chem*, **25B**, 391 (1934); Kistiakowsky, G. B., and Nelles, M., *Phys. Rev.*, **41**, 595 (1932).

[7] Klingstedt, F. W., *Compt. rend.*, **175**, 1065 (1922); see also Orndorff, W. R., Gibbs, R. C., McNulty, S. A., and Shapiro, C. V., *J. Am. Chem. Soc.*, **50**, 831 (1928); Shapiro, C. V., and Gibbs, R. C., *Phys. Rev.*, **31**, 310 (1928).

[8] Kwieninski, L., and Marchlewski, L., *Bull. Acad. Polonaise*, **A**, 255 (1929); *Chem. Abs.*, **24**, 783 (1930).

2490, 2433 and 2390A. The spectrum is of importance because it frequently appears in the absorption spectra of other not especially purified compounds of which benzene is a contaminant. As such, it has been erroneously reported as the absorption spectrum of substances, such as ether, contaminated by it. Indeed, the presence of small amounts of benzene vapor in the atmosphere can be detected and the benzene determined by drawing the air through alcohol and then taking the absorption spectrum. As little as 0.1 mg. per liter of air can be determined with an accuracy of about 5 per cent (in the absence of homologs) in a one liter sample.[9]

The absorption of the homologs of benzene has also been extensively studied.[10] In general, the addition of alkyl groups into benzene leads to a fusion, more or less complete, of the benzene bands.

Kailan [11] compared the action of radium and of ultraviolet rays upon toluene. The former changed less than 0.25 per cent of a sample of toluene exposed for two years. The products formed included benzaldehyde, benzoic acid, and apparently, formic acid. The principal product consisted, not of benzoic acid, but of a yellow, viscous mass composed presumably of hydrocarbons and of condensation products of benzaldehyde. Changes of a similar nature and order of magnitude were said to have been produced by 22 hours of exposure to the radiation from a quartz mercury lamp at a distance of 8 to 9 centimeters. In the presence of water, the action was slightly increased and some oxalic acid was also formed.

The fact that the most easily isolable products of the autoxidation in light of benzene homologs are carboxy-acids was attributed by Suida [12] to the relative stability of intermediate products. He believed that, with the quartz lamp as source, the velocity of the first stage of the oxidation could be approximately measured by the amount of peroxide formation, estimated by the liberation of iodine from acidified potassium iodide. The amount of carboxylic acid formed could not, however, be entirely due to the decomposition of peroxide. More recent workers have contributed to this work, but an understanding of the mechanism of the process is not complete.

The oxidation of xylene occurs more than twice as rapidly as that of toluene, para-xylene oxidizing more rapidly than the ortho isomer. The process is accelerated by the addition of small quantities of nitrobenzene, or of one of the nitrotoluenes.

According to Sudborough, Watson and Narayanan [13] it was claimed by Eckert [14] that 40 per cent yields of benzoic acid could be obtained in six weeks from toluene by atmospheric oxidation in sunlight in the presence of anthraquinone. In a repetition and extension of these experiments, Sudborough and co-workers used 200-cc. quartz flasks containing 50 gm. of toluene and 5 gm. of anthraquinone. The flasks were filled with oxygen and connected with a reservoir of that gas.

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[9] Laurian, P., *14me Congr. chim. ind. Paris*, Oct. 1934, 6 pp ; *Chem. Abs.*, **29**, 6173 (1935). For data on the absorption of solid benzene, see Pringsheim, P., *Physik. Z.*, **27**, 856 (1926). Kronenberger, A , and Pringsheim, P., *Z. Physik*, **40**, 75 (1926). For the Schumann region, see Price, W. C., and Wood, R. W., *J. Chem Physics*, **3**, 439 (1935).

[10] Pestemer, M., and Gubitz, O., *Monatsh.*, **64**, 426 (1934); Henri, V., and Walter E., *Compt. rend.*, **176**, 746 (1923); Conrad-Billroth, H., *Z. physik. Chem.*, **B29**, 170 (1935); Wolf, K. L., and Herold, W., *Z. physik. Chem.*, **B13**, 210 (1931); **B21**, 389 (1933); Radulescu, D , and Dragulescu, C., *Physik. Z.*, **36**, 66 (1935). Aubert, M., and Gheorghiu, T., *Ann. combustibles liquides*, **8**, 451 (1933); *Chem. Abs.*, **29**, 2448 (1935). Ramart-Lucas, Mme., and Amagat, P., *Compt. rend.*, **188**, 638 (1929); *Bull. soc. chim.*, **51**, 108 (1932); Horio, M., *J. Soc. Chem. Ind. Japan*, **37**, 135 (1934).

[11] Kailan, A., *Monatsh.*, **40**, 445 (1920); *J. Chem. Soc.*, **118**, i, 538 (1920).

[12] Suida, H., *Monatsh.*, **33**, 1255 (1912).

[13] Sudborough, J. J., Watson, H. E., and Narayanan, B., *J. Indian Inst. Sci.*, **8A**, 1 (1925); British P. 182,487; *J. Soc. Chem. Ind.*, 782 (B.1925); John, H., *Ber.*, **58B**, 1563 (1925).

[14] Eckert, A., Indian P. 8425; *Ber.*, **58B**, 313 (1925).

They were rocked at such a rate that the liquid was continuously splashed over the upper part of the interior surface exposed to the light. The temperature was 63-6° C. when the source was a mercury arc and 29-50° C. when sunlight was employed. The amount of acid determined by titration always exceeded that which could be isolated as benzoic acid, probably because of the formation of some formic acid. The amount of acid formed was roughly proportional to the time of exposure and was markedly dependent upon the amount of water present. The yield of acid in sunlight ranged from 0.76 per cent with 2.5 gm. water and 2.03 per cent with 25 gm. of water after 60 hours to 6.60 and 17.3 per cent, respectively, after 400 hours. In ultraviolet light, the values were: after 200 hours, 4.7 per cent with 2.5 gm. water and 15.7 per cent with 25 gm. water and, after 600 hours 16.3 and 34.7 per cent. The addition of nitrobenzene as catalyst had practically no effect. The presence of oxygen was essential. Meta-xylene and mesitylene showed no marked oxidation after 200 hours of ultraviolet treatment. It was found by Castiglioni [15] that one and a half times as much benzoic acid was formed in a given time when Uviol flasks were used as when ordinary glass flasks were employed.

The discrepancy between the reports regarding the effect of nitrobenzene may have been due to a slow photoreaction between toluene and nitrobenzene which occurs even under nitrogen and in the absence of anthraquinone. Vecchiotti and Zanetti [16] find that a large quantity of nitrobenzene (100 gm.) and 20 gm. of toluene give, after six months in sunlight, 20 gm. of benzoic acid and *p*-aminophenol. This indicates that the side-chain of the toluene is oxidized and that the nitrobenzene is reduced to aminophenol. This reaction had been observed previously by Ciamician and Silber.[17]

Subsequent observations of the anthraquinone-sensitized oxidation of toluene by Kothari and Watson [18] indicated the rate to be greatest in the presence of 1 per cent of catalyst. The rate is initially slow, but gradually speeds up and eventually becomes constant. They believed the fraction of toluene oxidized, 8.3 to 9.8 per cent, to be larger in proportion to time when the sun was the source than when the mercury arc was employed. Uranium salts had irregular effects as catalysts.[19]

Xylene mixed with an aromatic nitro-hydrocarbon is reported to contain more active oxygen after exposure to light and oxygen than pure xylene exposed to light and oxygen, but Suida [20] found that the presence of a nitro- compound reduced the total yield of oxidation product, although considerable quantities of toluic aldehyde were present. Thus in the presence of a nitro-hydrocarbon the less stable products of oxidation (aldehydes and peroxides) remained, while the pure chemical reaction (the decomposition of these primary products to the next higher and more stable stage of oxidation) was delayed. It was possible by cooling in carbon dioxide and ether to bring almost to a standstill the decomposition of the benzene hydroperoxide (formed from benzaldehyde by the action of ultraviolet). The product of the primary autoxidation process could not be isolated, as it decomposed into benzoic acid within a few minutes after removing it from the cooling mixture. Little is known as yet regarding the mechanisms of these oxidations.

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[15] Castiglioni, A., *Gazz. chim. ital.*, **63,** 818 (1933); *Brit Chem. Abs*, **A,** 264 (1934); see, however, John, H., *Ber.*, **58B,** 1563 (1925); *Chem. Abs.*, **20,** 337 (1926).

[16] Vecchiotti, L., and Zanetti, G., *Gazz. chim. ital.*, **60,** 479 (1930); *Chem. Abs.*, **25,** 251 (1931).

[17] Ciamician, G., and Silber, P., *Gazz. chim. ital.*, **33,** 354 (1903); **36,** 174, 176, 190, 197 (1906).

[18] Kothari, C. J., and Watson, H. E., *J. Indian Inst. Sci.*, **A14,** 11 (1931); *Chem. Abs.*, **26,** 378 (1932).

[19] See also Nozicka, F., U. S. P 1,945,067, Jan. 30, 1934; *Chem. Abs.*, **28,** 2273 (1934); German Patent 624,964; *Chem. Abs.*, **30,** 4870 (1936); and Kreidl, I., U S. P. 1,971,042, Aug. 21, 1934, for other catalysts related to anthracene or anthraquinone.

[20] Suida, H., *Ber.*, **47,** 467 (1914); *Monatsh. Chem.*, **33,** 1268 (1912).

Plotnikow[21] notes that sunlight acts on solutions of potassium dichromate containing various organic compounds. Triphenylmethane is unaltered and benzene remains almost unchanged even in the presence of ferric chloride, but toluene yields a variety of products. Phenol forms benzoquinone and a mixture of polyhydric phenols. Ortho- and meta-xylenes yield tolualdehydes and acids, and some formic acid is formed from *p*-xylene. Quinol forms primarily benzoquinone, but phthalic acid also has been isolated from the reaction products. Resorcinol and pyrocatechol yield trihydric phenols, benzoquinone and similar compounds. A solution containing *o*-cresol decomposes with evolution of carbon dioxide and separates into two layers, of which the lower contains unchanged cresol, chromic hydroxide, and a tarry substance, and the upper, benzoic and oxalic acids. Naphthalene and α-naphthol are unchanged after ten months of irradiation. Some aniline dyes give fluorescent solutions. Aniline is converted rapidly into aniline black, and *p*-aminophenol into benzoquinone and ammonia. Results with pseudocumene indicate that the possibility of terpene formation is dependent on a symmetrical molecular structure. Dihydroxyanthraquinone breaks down into benzoquinone and carbon dioxide. Mixtures of isopulegol and ammonium dichromate in various proportions yield on irradiation in aqueous or alcohol solutions only about 1 per cent of isopulegone, whereas isoeugenol undergoes extensive oxidation.

Substitution Products of Benzene. Although the absorption spectra of the various halogen substitution products of benzene and its homologs have been recorded and in some cases analyzed,[22] little is known regarding their photochemical decompositions or reactions.

Without catalysts, *p*-bromobenzenesulfonate undergoes no decomposition in darkness and less than 2 per cent in light.[23] In the presence of charcoal, 0.65 to 0.95 per cent decomposition occurred in darkness and 2.28 to 3.21 per cent in the light of a carbon arc. The corresponding values in the presence of copper were 3.78-5.26 and 5.83-7.79 per cent. In the presence of both copper and charcoal, the values were 10.71 to 23.70 per cent decomposed in darkness and 14.29 to 26.28 per cent in light.

PHOTOCHEMICAL NITRATIONS AND NITRO- COMPOUNDS

In the photochemical reaction in sunlight between benzene and a mixture of nitric and sulfuric acids, Sollazzo[24] finds that there are successively formed nitrobenzene, nitrosobenzene, azoxybenzene and finally the salts of azoxybenzenesulfonic acid.

Bass and Johnson[25] allowed nitrogen peroxide to react with benzene for three months in sealed tubes both in darkness and in sunlight. The only nitration products identified were the mono- and di-nitroderivatives, formed in very small yield. Anhydrous nitrogen peroxide gas was passed over 50 gm. of dry toluene in a water-cooled quartz tube exposed to a quartz mercury arc for six hours. In addition to 2.5 gm. of benzoic acid and 32.0 gm. of toluene, there was obtained 13.0 gm. of an unstable low-boiling (40-80°C.) liquid which showed no definite boiling point, but decomposed into toluene and nitrogen peroxide. They believed the nitrogen peroxide to act solely as an oxidizing agent, practically no nitration taking place.

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[21] Plotnikow, J., *Chem Ztg.*, **52**, 669 (1928); *Chem. Abs.*, **22**, 4380 (1928).

[22] Errera, J., and Henri, V., *J. Phys Radium*, **9**, 205, 249 (1928); Conrad-Billroth, H., *Z. physik. Chem.*, **B19**, 76 (1932); **B25**, 139, 217 (1934); Klingstedt, F. W., *Z. physik Chem.*, **20B**, 125 (1933).

[23] Sandonnini, C., *Atti R. Accad. Lincei*, **2**, 427 (1925); *Chem Abs.*, **20**, 1018 (1926).

[24] Sollazzo, G., *Officina*, **4**, 268 (1931); *Chem. Abs.*, **26**, 1862 (1932).

[25] Bass, L. W., and Johnson, T. B., *J. Am. Chem. Soc.*, **46**, 456 (1924).

More recently, however, it was found[26] that when 40 gm. of toluene were passed in vapor form with 180 to 200 gm. of nitrogen peroxide and 45 to 50 liters of carbon dioxide at 14° to 15°C. during two hours before or through a jacketed quartz mercury-vapor lamp, 55 per cent of the toluene reacted, giving about 5 gm. of the side-chain nitration product, and 27-28 gm. of a mixture of mononitrotoluenes. No dinitrotoluene and no benzoic acid were produced. Raising the temperature to 58-60°C. did not affect the side-chain nitration, but lowered the yield of the nitrotoluenes to 15 gm. In the absence of radiation, less toluene reacted, but the relative amounts of side-chain and nuclear substitution were but little affected. The nitration of benzene was but little affected by irradiation. Titov and Baryshnikova[27] obtained rather similar results under conditions, such as low concentration and illumination, which favored the dissociation of the N_2O_4. They did observe a considerable amount of disubstitution in the side chain, as well as some benzaldehyde and benzoic acid formation. These products were secured in the absence of illumination. In sunlight or the light of the mercury arc, all the reactions were accelerated except that the ring substitution was reduced approximately 4 to 9 per cent.

Irradiation has little effect on the nitration of benzene, *n*-hexane or cyclohexane. In general, it is helpful only when the completely symmetrical structure of the benzene molecule is disturbed by the presence of a side-chain.[28]

To obtain information regarding the photochemical action of nitrobenzene on various organic compounds, a field already investigated by Ciamician and Silber,[29] Vecchiotti and Zanetti[30] exposed it in an atmosphere of nitrogen to sunlight for six months in contact with the substance to be tested. In the reaction with cinnamic acid, the products obtained included benzoic acid, carbon dioxide, benzanilide, azoxybenzene and hydroxyazobenzene. It was assumed that the double bond of the cinnamic acid was ruptured, with the formation of benzaldehyde and OHCCOOH, these products being oxidized to benzoic and oxalic acids. On further oxidation, cinnamic acid yields carbon dioxide. The nitrobenzene is reduced to nitrosobenzene. The formation of the remaining three compounds is accounted for by reference to the explanation given by Ciamician and Silber[31] for the action of nitrobenzene on benzaldehyde. Benzanilide may be formed from benzaldehyde by either of the reactions:

$$C_6H_5NO_2 + 3C_6H_5CHO \longrightarrow C_6H_5NHCOC_6H_5 + 2C_6H_5COOH.$$
$$C_6H_5NO + 2C_6H_5CHO \longrightarrow C_6H_5NHCOC_6H_5 + C_6H_5COOH.$$

Azoxybenzene may be formed by

$$2C_6H_5NO + C_6H_5CHO \longrightarrow C_6H_5N(:O):NC_6H_5 + C_6H_5COOH.$$

or by analogy with the Bamberger[31a] reaction of nitrosobenzene and C_6H_5HNOH by

$$C_6H_5NO + C_6H_5(HO)NCOC_6H_5 \longrightarrow C_6H_5N(:O):NC_6H_5 + C_6H_5COOH.$$

[26] Schorigin, P., and Toptschiev, A., *Ber.*, **67**, 1362 (1934); *J. Gen. Chem. Russ*, **5**, 549 (1935), *Brit. Chem. Abs.*, **A**, 61 (1936).

[27] Titov, A. I., and Baryshnikova, A. N., *J. Gen. Chem. U.S.S.R.*, **6**, 1801 (1936); *Chem. Abs.*, **31**, 4285 (1937).

[28] Schorigin, P., and Toptschiev, A., *loc. cit.*, for attempts at substitution of hydrocarbons by NOCl during irradiation, see Perrot, R., *Compt. rend.*, **198**, 1424 (1934).

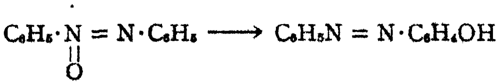
[29] Ciamician, G., and Silber, P., *Gazz. chim. ital.*, **33**, 354 (1903); **36**, 174, 176, 190, 197 (1906)

[30] Vecchiotti, L., and Zanetti, G., *Gazz. chim. ital.*, **60**, 479 (1930); *Chem. Abs.*, **25**, 251 (1931).

[31] Ciamician, G., and Silber, P., *Compt. rend. Acad. Lincei*, **14**, 265 (1905).

[31a] *Ber.*, **35**, 1606 (1902).

The last of the three compounds may be formed from $C_6H_5N(:O):NC_6H_5$ by transposition.[82]



$$C_6H_5 \cdot \underset{\underset{O}{\|}}{N} = N \cdot C_6H_5 \longrightarrow C_6H_5N = N \cdot C_6H_4OH$$

or by

$$C_6H_5NO + C_6H_4(OH)NH \cdot COC_6H_5 \longrightarrow HO \cdot C_6H_4N = NC_6H_5 + C_6H_5COOH$$

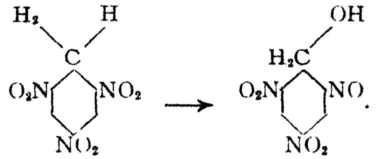
Even in darkness, cinnamic acid and nitrobenzene gave benzoic acid and azoxybenzene.

In the photochemical reaction of nitrobenzene and naphthalene, a trace of β-naphthol was the only product identified.

On exposure to sunlight, Sollazzo[33] found a mixture of ethanol, ammonium hydroxide and *m*-dinitrobenzene to become red-yellow. In the case of amyl alcohol, the color was cherry-red; it was permanent in darkness.

Illumination of 1-styryl-3-bromostyryl-4, 6-dinitrobenzene gives 2-phenyl-5-styryl-6-nitroisatogen.[34]

Molinari and Giua are said[35] to have observed 2,4,6-trinitrotoluene to turn slowly brown on the surface when exposed to bright daylight. The melting point dropped from 80° to 74° in three months. Custis[36] found that a more rapid reaction occurs when the material was exposed to an iron arc, but a mercury arc did not prove effective. Schultz and Ganguly[37] attribute the red coloration observed after the prolonged action of light on 2,4,6-trinitrotoluene in the presence of oxygen, hydrogen, nitrogen or *in vacuo*, to the production of two tautomeric quinonoximes, $C_7H_5O_6N_3$, of melting points above 280°C. They can be separated by their differing solubilities in cold acetone. Each dyes wool red. They are considered to be 2-nitro-6-nitroso 5-hydroxymethyl-*p* benzoquinone-4-oxime and 2-nitro-4-nitroso-5-hydroxymethyl-*o*-benzoquinone-2-oxime. The course may involve the migration of an oxygen atom from a nitro- group to the methyl group, as in



In acetone solution, the process may stop here, the product melting at 108-111°C. In the case of the solid, a repetition of the process yields the unstable 4-nitro-2,6-dinitrosodihydroxymethylbenzene. One hydroxyl migrates to the nucleus, and then passes its hydrogen to one or the other nitroso- group, forming the *o*- and *p*-oximes. The assumption that only the nitro- groups in the 2 and 6 positions are reduced is supported by the observation that 2,6 dinitrotoluene is converted by exposure to light into a yellow substance, probably 2,6-dinitroso-4-hydroxybenzyl alcohol, although *p*-nitrotoluene is completely unchanged. The presence of a nitro- group in the *para* position appeared to retard the change, since 2,4-dinitrotoluene is almost stable to light. 2,4,6-Trinitrobenzyl alcohol in benzene and 2,4,6-trinitrobenzyl bromide, as a solid or in benzene, are also sensitive to light.

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[82] Knipscheer, H. M., *Rec. trav. chim.*, **22**, 14 (1903).

[33] Sollazzo, G., *Officina*, **4**, 340 (1931); *Chem. Abs.*, **26**, 3729 (1932); *Boll. chim farm*, **72**, 913 (1933); *Brit. Chem. Abs.*, **A**, 264 (1934); *Chem. Abs.*, **28**, 5758 (1934).

[34] Ruggli, P., and Zimmerman, A., *Helv. Chim Acta*, **15**, 865 (1932); *Chem. Abs.*, **27**, 292 (1933).

[35] Escales, R., "Die Explosivstoffe mit besonderen Berüchsightigung der neueren Patente." *Heft*, **6**, "Nitrosprengstoffe," p. 295. Leipzig, Vereinigg. wissensch. Verleger, 1915.

[36] Custis, H. H., *J. Frank. Inst.*, **184**, 876 (1917); *Chem. Trade J.*, **62**, 90; *Chem. Zentr*, 208, I (**1928**).

[37] Schultz, G., and Ganguly, K. L., *Ber.*, **58B**, 702 (1925).

It was believed by Krauz and Turek [38] that exposure of trinitrotoluene in thin layers to sunlight increased its sensitiveness to shock. This was attributed to a decomposition leading to the formation of both picric and trinitrobenzoic acids. Metals or metal oxides were supposed to hasten this change, which occurred to a sufficient extent to change the melting point in four months from 81.4° to 73.5°C. These results have been critically examined by Wichart and Donat [39] and by Lodati,[40] who find the technical products completely stable in contact with metals. The latter worker states, however, that in diffused light, the compound formed some nitrous vapors in three months [41]

According to Sachs and Hilpert,[42] the nitrobenzylidene group should be light-sensitive. This was confirmed by I. and H. Tănăsescu [43] in studies of the action of sunlight on *o*-nitrobenzylideneglycol, $\underline{O\cdot CH_2\cdot CH_2\cdot O\cdot CH}\cdot C_6H_4NO_2$, which yielded a white crystalline isomer *o*-$NO\cdot C_6H_4\cdot \underline{C(OH)\cdot O\cdot CH_2\cdot CH_2O}$, melting at 128°C. to a green liquid which readily hydrolyzed on boiling with acid or base to form glycol and *o*-nitrosobenzoic acid. A similar migration of oxygen from a nitro-group to form an alcohol group (mentioned by Schultz and Ganguly in the case of trinitrotoluene) was observed in di-*o*-nitrobenzylideneerythritol. A similar type of behavior is also encountered in the case of *o*-nitrobenzaldehyde. Tănăsescu and Macovski [44] have extended this work to include the changes in 1,2,5,6-di-*o*-nitrobenzylidenedulcitol which gives a resin, possibly by partial isomerization and *p*-nitrobenzylidene-3-benzoylglycerol. Included are also the *o*-nitrobenzylidene-acetals of a number of other glucides, such as mannitol and sorbitol. The structure of the photochemical isomerization products was not definitely established, these authors believing an open-chain formula of the type $O\text{-}ROCH_2CH_2OCOC_6H_4NO$ the most adequate. Recently, the corresponding compounds of galactose, α-methyl-galactose, mannose, rhamnose, fructose, lactose and sucrose have been found to give isomerizations when irradiated in chloroform and benzene solutions.[45]

BENZALDEHYDE

Although benzaldehyde is thermally decomposed only at temperatures of 400°C. and higher, wave-lengths shorter than 2600A (more accurately 2438A) produce a photolysis at room temperature, according to de Hemptinne.[46] He believed the primary products to be carbon monoxide, a phenyl radical and a hydrogen atom, the latter combining to produce benzene. The energy necessary for this was calculated to be 115.7 kcal., corresponding to 2461A, at which the "total" absorption band of the benzaldehyde spectrum begins.

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[38] Krauz, C., and Turek, O., *Z. ges. Schiess-u. Sprengstoffw.*, **20**, 49 (1925); *Chem. Abs.*, **19**, 2747 (1925); *Chem. Age (London)*, **13**, 392 (1925); *Chem. Abs.*, **20**, 824 (1926)

[39] Wichart and Donat, *Z. ges. Schiess-u. Sprengstoffw.*, **20**, 69 (1925)

[40] Lodati, D., *Giorn. Chim. Ind. Appl.*, **7**, 572 (1925); *Chem. Abs.*, **20**, 3815 (1926); but see also, Sucharevskii, M., *Z. ges. Schiess-u. Sprengstoffw.*, **20**, 40 (1927); *Chem. Abs.*, **21**, 3462 (1927)

[41] For spectrographic studies of this reaction, see also Pavlik, M., *Chimie et Industrie, Special No.*, 245 (June, 1933)

[42] Sachs, F., and Hilpert, S., *Ber.*, **37**, 3425 (1904).

[43] Tănăsescu, I., and Tănăsescu, H., *Bul. soc. stiinte Cluj*, **2**, 369 (1925), *Chem. Abs.*, **20**, 749 (1926).

[44] Tănăsescu, I., and Macovski, E., *Bull. soc. chim.*, **53**, 1097 (1933); *Chem. Abs.*, **28**, 1330 (1934), *Bull. soc. chim.*, **51**, 1371 (1932); *Chem. Abs.*, **27**, 1874 (1933), *Bull. soc. chim.*, **51**, 1556 (1932), *Chem. Abs.*, **27**, 2142 (1933), *Bull. soc. chim.*, **45**, 1022 (1929); *Chem. Abs.*, **24**, 2118 (1930); *Bull. soc. chim.*, **47**, 86 (1930), *Chem. Abs.*, **24**, 2429 (1930); *Bull. soc. chim.*, **47**, 457 (1930); *Chem. Abs.*, **24**, 4270 (1930).

[45] Tănăsecu, I., and Craciunescu, E., *Bull. soc. chim.*, **3**, 581 (1936); Tanasescu, I., and Jonescu, M., *Bull. soc. chim.*, **3**, 1517 (1936).

[46] de Hemptinne, M., *Compt. rend.*, **186**, 1295 (1928); *Ann. Soc. Sci. Bruxelles*, **48B**, 98 (1928), *Brit. Chem. Abs.*, **A**, 409 (1929); *J. Phys. Radium*, **9**, 357 (1928).

The absorption spectrum has been studied recently by Almasy[47] who found three broad regions. From 3747 to 3163A, there were 159 measurable bands in the vapor; between 2963 and 2599A there were 51. At 2428 to 2349, there were six bands followed by continuous absorption. As the temperature is raised, the character of the spectrum is altered, the narrow bands fusing into broader ones indicating the occurrence of predissociation at longer wave-lengths, the higher the temperature. At 208°C the fine bands present at lower temperatures between 2966 and 1610A are continuous and radiations in this range produce photolysis. At 270°C radiations shorter than 3200A produce dissociation.

On exposure to ultraviolet rays, hexahydrobenzaldehyde yields carbon monoxide, cyclohexane and the dimer.[48] Phenylacetaldehyde does not evolve carbon monoxide, but is partly converted into a yellow oil and a brownish-red, viscous residue. Hydrocinnamaldehyde also is said to be practically unaffected by ultraviolet light. Hexahydrophenylacetaldehyde yielded a gas containing 88 per cent of carbon monoxide, hexahydrotoluene, and small quantities of polymerized products.[49] Hexahydro-β-phenylpropaldehyde, after ten hours' exposure to ultraviolet, gave carbon monoxide more slowly and in smaller quantity and highly polymerized products from which only a trimer of the original aldehyde, but no hexahydroethylbenzene, could be isolated.

Oxidation of Benzaldehyde It was early claimed[50] that the autoxidation of either benzaldehyde or of pinene under the influence of rays from a Uviol lamp increased the electrical conductivity of oxygen. It had been found by Jorissen and Ringer[51] that when a mixture of one mole of benzaldehyde and two of acetic anhydride is exposed to the diffused light of an arc or a magnesium flame in an atmosphere of oxygen in a closed vessel, benzoylacetal peroxide could be obtained.

Suida[52] passed a current of oxygen through a solution of benzaldehyde in petroleum ether (cooled with ice), while irradiating it by a Heraeus quartz lamp at a distance of two centimeters. After six hours a considerable amount of benzoic acid and small quantities of a peroxide were found, which could not be readily isolated When the vessel was cooled by means of solid carbon dioxide and ether, the formation of the peroxide was much increased and a white deposit with strong oxidizing properties and a pungent odor was obtained.

By a combination of iodometric and acidimetric titrations during the reaction, Bäckström[53] found that perbenzoic acid is the product of the photochemical reaction. The quantum efficiency is high, of the order of 10,000. The reaction can be inhibited. The perbenzoic acid subsequently reacts with benzaldehyde, forming benzoic acid by a pseudo-unimolecular thermal reaction, which shows little or no negative catalysis. This reaction is accelerated by light, but the quantum yield is less than 0.5 per cent of that of the reaction by which the perbenzoic acid is formed. The quantum yield for the total reaction, measured by the oxygen uptake, decreases during the progress of the reaction.

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[47] Almasy, F., *J. chim. phys.*, **30**, 528, 713 (1933).

[48] Franke, A., and Sigmund, F., *Monatsh*, **46**, 61 (1925); *cf* also Wallach, O, and Isaac, E., *Annalen*, **347**, 331 (1906).

[49] Sigmund, F., *Monatsh.*, **52**, 185 (1929).

[50] Jorissen, W. P., and Vollgraff, J. A., *Chem. Weekblad*, **12**, 93 (1915); *J. Chem Soc.*, **108** (ii), 80 (1915).

[51] Jorissen, W. P., and Ringer, W. E., *Chem. Weekblad*, **2**, 19; *Chem Zentr*, **76**, 817 (1905).

[52] Suida, H., *Ber*, **47**, 471 (1914).

[53] Bäckström, H., *Med K. Vetenskapsakad. Nobelinst*, **6**, Nos 15 and 16 (1927); Bäckström, H., and Beatty, H. A., *J. Phys. Chem.*, **35**, 2530 (1931).

According to Kothari and Watson[54] this decrease, which is found also in toluene solutions and by the use of an incandescent light source, is greater than could be accounted for by the retarding action of the benzoic acid. It was less when benzene was the solvent. Anthraquinone may serve as an accelerator of the reaction when toluene is the solvent, but is not effective in benzene. Benzoquinone is a strong inhibitor, and phenolic compounds also act in this way. According to Jorissen and Dekking,[55] the photoöxidation of benzaldehyde in the presence of iodobenzene induces oxidation of the latter compound.

Photochemical reactions between aldehydes and quinones have been the subject of a number of empirical observations.[56] Angeletti and Baldini,[57] found that after exposure to sunlight for six months an equimolar mixture of benzaldehyde and toluquinone in benzene gave benzoic acid, toluhydroquinone, a relatively small quantity of diethyl toluhydroquinone benzoate, an unidentified phenolic compound, and large quantities of resins. Light reduced the toluquinone to toluhydroquinone and oxidized the benzaldehyde to benzoic acid. The latter then esterified the two hydroxyl groups of toluhydroquinone. Cinnamaldehyde and toluquinone similarly gave cinnamic acid, toluhydroquinone and a monocinnamate of toluhydroquinone.[58] No compounds corresponding to the 2,5-dihydroxybenzophenone were reported by Klinger.[59]

It has been stated by Chattaway[60] that benzaldehydephenylhydrazone reddens slowly in diffused light. In sunlight, the change becomes very noticeable in a few minutes, reaching, in a few hours, a maximum intensity, the crystals having a brilliant scarlet color like that of azobenzene. The change could be produced also by the light of an iron arc, but the ultraviolet rays were not held responsible since the interposition of glass did not interfere with the effect. Hodgson and Handley[61] found no change in the phenylhydrazone of *p*-nitrobenzaldehyde under similar treatment.

Transformation of o-Nitrobenzaldehyde. The nature of the isomerization which occurs when this compound is irradiated either as a solid or in acetone solution is similar to that described on page 472 for the *o*-nitrobenzylidene glycols. An oxygen atom is removed from the nitro- group and transferred to the aldehyde group, forming in this case *o*-nitrosobenzoic acid. Weigert and Kummerer[62] showed that the amount of the reaction is proportional to the time of irradiation. In experiments in which the intensity was varied, they believed that their data indicated a slight deviation from the Bunsen-Roscoe law. When ultraviolet light was employed, the rate of the change was independent of the concentration, but when violet light was used the rate was at first proportional to the concentration.

In later work, the quantum yield was found[63] to be 0.5 when the wave-lengths 4360, 4050 or 3660A were used. To account for this, they developed a special theory in which the orientation of the molecules with respect to the electric vector of the incident light was considered a determining factor. It was suggested that the transfer of an oxygen atom to an aldehyde group takes place only when the electric vector of the incident radiation corresponds to the line between the nitro- and aldehyde groups. It could be shown that only 50 per cent of the molecules would be so oriented as to react. Thus, for these molecules, the quantum yield would be unity, although the observed value was but 0.5. Such a theory lost its significance when it was found that many reactions in solutions have quantum yields varying in exact value, but less than unity. Furthermore, it has been found by some that Weigert's results [64] showed some variations from the 0.5 which his theory demands, as various wave-lengths were employed. This, however, has been denied by Weigert and Pruckner [65] after further observations. The value of 0.5 has been verified also by Leighton and Lucy [66] for 2,4-dinitrobenzaldehyde as well as for *o*-nitrobenzaldehyde. They found somewhat higher values in the case of 2,4,6-trinitrobenzaldehyde.[67] These, as well as other recent workers [68] reject the Weigert theory, and believe the usual explanations given for low quantum yields in liquid or solid-phase reactions to apply. Leighton and Lucy related the yield of 0.5 to the assumption that the N=O adjacent to the aldehyde group must be excited for the transformation to occur. They consider the processes of energy exchange between the two N=O linkings.

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[54] Kothari, C. J., and Watson, H. E., *J. Indian Inst. Sci.*, **A14**, 11 (1931); *Chem. Abs*, **26**, 378 (1932).

[55] Jorissen, W. P, and Dekking, A. C. B, *Rec. trav. chim*, **57**, 829 (1938).

[56] Ciamician, G., and Silber, P, *Ber*, **24**, 1430 (1891); **31**, 124 (1898), Klinger, H, *Annalen*, **249**, 137 (1888); Bargellini, G., and Monti, L., *Gazz chim. ital*, **60**, 474 (1930); *Chem Abs.*, **25**, 96 (1931).

[57] Angeletti, A., and Baldini, V., *Gazz. chim. ital.*, **64**, 346 (1934); *Chem. Abs*, **28**, 5422 (1934).

[58] Angeletti, A., *Atti accad sci., Torino, Classe sci. fis, mat. nat.*, **70**, 326 (1935); *Chem. Abs.*, **30**, 1383 (1936); *Atti V Congr. Naz Chim.*, **1**, 280 (1936); *Brit. Chem. Abs*, **A** (II), 196 (1937).

[59] Klinger, H., *Annalen*, **382**, 211 (1911); *Chem. Abs.*, **5**, 3456 (1911).

[60] Chattaway, F. D., *J. Chem. Soc.*, **89**, 463 (1906).

[61] Hodgson, H. H., and Handley, F. W., *J. Chem. Soc.*, 1882 (1928).

[62] Weigert, F., and Kummerer, L., *Ber.*, **46**, 1207 (1913); see also Bowen, E. J., Hartley, H., Scott, W. D., and Watts, H. G., *J. Chem. Soc.*, **125**, 1218 (1924).

[63] Weigert, F., and Brodmann, L., *Trans. Faraday Soc.*, **21**, 453 (1926).

Janssen found the absorption spectrum of the vapor of this compound to be continuous, implying a primary photodecomposition. Zimmer, who noted the compound to be dichroic at 4360 and 4050A although not a mixture of two tautomers, found it to exhibit no appreciable fluorescence. He believed that the primary process produces nitrosobenzaldehyde and an oxygen atom. The latter could recombine with the other dissociation product in either of two ways—to restore the original compound or to form the nitrosobenzoic acid. The equal likelihood of these two processes would account for the quantum yield of 0.5. Küchler and Patat [69] found the quantum yield in the gas phase to be much higher than that in solution. At 90°C., it reached 0.75, but could be lowered to 0.5 by the presence of 700 mm. nitrogen. They did not accept the theory of a primary splitting off of oxygen and could find no evidence for the primary formation of oxygen atoms. Neither free oxygen nor nitric oxide was formed. They believed the simplest explanation of the quantum yields of 0.5 to be a deactivation of some type of excited molecule, regulated intramolecularly.

Various other compounds, as has already been indicated, undergo a similar type of transformation. Tănăsescu [70] believes all substances which contain the *o*-nitrobenzaldehyde grouping and which are light-sensitive contain a mobile hydrogen atom. An example of a light-insensitive compound is *o*-nitrocinnamaldehyde. In this case, according to Kögel, the aldehyde group differs in not being an oxygen-acceptor.[71] In the presence of pyrogallol as oxygen acceptor, however, the nitro- group of this aldehyde, as well as that of *o*-nitrobenzaldehyde, is light-sensitive. In the case of nitroterephthaldehyde, the maximum quantum yield in the transformation into 2,4,1-nitrosoterephthaldehydic acid in acetone solution is 0.1 in light of the ranges 3740-3251 and 3740-3345A. With light of constant intensity, the rate of reaction diminishes as exposure continues. It increases with increasing light intensity, approaching a limit. Kögel assumes that before exposure the normal molecules of the aldehyde are in equilibrium in solution with an intermediate substance, and that it is this substance which reacts photochemically with the normal molecules. This conclusion, which he applies also to *o*-nitrobenzaldehyde, was based upon an observed diminution of the absorption coefficients of the solution with rise in temperature. This was ascribed to the formation of a substance with relatively small absorption coefficients.

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[64] Weigert, F., and Pruckner, F., *Z. physik. Chem. Bodenstein-Festband,* 775 (1931); Weigert, F., (1929).

[66] Leighton, P. A., and Lucy, F. A., *J. Chem. Physics,* **2,** 756, 760 (1934).

[67] See also Secareanu, S., and Lupas, I., *Bull. soc. chim.,* **3,** 1161 (1936); *Brit. Chem. Abs.,* **A,** 986 (1936).

[68] Wegscheider, R., *Monatsh.,* **52,** 68 (1929); Janssen, C., *Z. physik Chem.,* **B18,** 241 (1932); Zimmer, K. G., *Ibid.,* **B23,** 239 (1933); Bowen, E. J., *Trans. Faraday Soc.,* **21,** 523 (1926).

[69] Küchler, L., and Patat, F., *Monatsh.,* **68,** 275 (1936); *Z. Elektrochem.,* **42,** 529 (1936).

[70] Tănăsescu, I., *Bull soc. chim.,* **39,** 1443 (1926).

[71] Kögel, J., *Z. wiss. Phot.,* **24,** 216 (1926); *Chem. Abs.,* **20,** 3646 (1926).

Davies[72] notes that 5-nitro-2-methoxy-3-ethoxybenzaldehyde undergoes no change of color or melting point when exposed in pure acetone solution for 25 hours to ultraviolet rays. On the other hand, another nitration product (melting point 85°C.) of 2-methoxy-3-ethoxysalicylaldehyde obtained by precipitation with water rapidly becomes greenish-blue under the same conditions.

AROMATIC KETONES

Ciamician and Silber[73] showed that when an alcoholic solution of benzophenone is exposed to sunlight, the ketone is reduced to benzopinacol and the alcohol is oxidized to aldehyde. Cohen[74] extended the observations to include a number of substituted ketones and a variety of primary and secondary alcohols. Böeseken, Cohen and Langedijk[75] gave data on the absorption of benzophenone, fluorenone and terephthalophenone for the region 3600 to 4500A and pointed out that their maximum absorption did not occur in the wave-length region which was photochemically active.[76]

To throw light on the nature of the primary reaction involved, Böeseken and Visser[77] determined the photoelectric threshold of benzophenone and found it to lie between 3025 and 2537A. The absorption band at 2600A would seem, therefore, to correspond to ionization of the molecule, a process unusually encountered in photochemical processes. No absorption bands were found in the region of excitation, 4070 to 3800A.

Having shown that a small amount of sodium alcoholate can effect the decomposition of a large amount of benzopinacol into a mixture of benzohydrol and benzophenone, Bachmann[78] combined this reaction with the photochemical reaction by conducting the latter in solutions containing a small amount of sodium alcoholate. The ketone regenerated in the decomposition of the pinacol into hydrol and ketone goes through the photochemical change again, and the series of reactions is repeated until eventually the hydrol is the sole product. In the case of benzophenone and isopropyl alcohol, the reactions are:

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[72] Davies, W. *J. Chem. Soc*, **123,** 1590 (1923)

[73] Ciamician, G., and Silber, P, *Ber*. **33,** 2911 (1900).

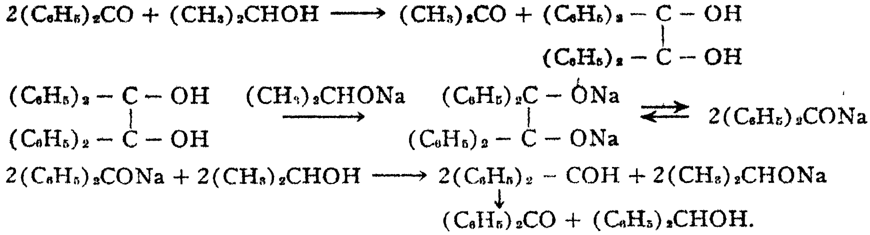
[74] Cohen, W. D., *Rec. trav. chim*, **39,** 242 (1920)

[75] Böeseken, J., Cohen, W. D, and Langedijk, S. L, *Rec. trav. chim*, **44,** 173 (1925), **46,** 383 (1927).

[76] For more recent data on the absorption of benzophenone and other ketones, see Tasaki, T., *Acta Phytochim.*, **2,** 49, 199 (1925); **3,** 259 (1927); Anderson, L. C, *J Am Chem Soc.*, **55,** 2094 (1933), Anderson, L. C., and Gooding, C. M., *J. Am Chem. Soc.*, **57,** 999 (1935); Purvis, J. E., *J. Chem. Soc.*, **127,** 9 (1925), Rupe, H, Collin, A., and Schmiderer, L., *Helv. Chim. Acta,* **14,** 1340 (1931), Rupe, H, Pedrini, F., and Collin, A., *Helv. Chim. Acta,* **15,** 1321 (1932); Rupe, H., Collin, A., and Sigg, W, *Helv. Chim. Acta*, **14,** 1355 (1931), Ley, H., and Wingchen, H., *Ber.*, **67B,** 510 (1934).

[77] Böeseken, J., and Visser, G. H., *Rec. trav. chim.*, **47,** 1037 (1928); *Chem. Abs.*, **23,** 2660 (1929).

[78] Bachmann, W. E., *J. Am Chem. Soc.*, **55,** 355, 391 (1933).



$$2(C_6H_5)_2CO + (CH_3)_2CHOH \longrightarrow (CH_3)_2CO + \begin{array}{l}(C_6H_5)_2-C-OH\\ \qquad\quad\;\; |\\ (C_6H_5)_2-C-OH\end{array}$$

$$\begin{array}{l}(C_6H_5)_2-C-OH\\ \qquad\quad\;\; |\\ (C_6H_5)_2-C-OH\end{array} \xrightarrow{(CH_3)_2CHONa} \begin{array}{l}(C_6H_5)_2C-ONa\\ \qquad\quad\;\; |\\ (C_6H_5)_2-C-ONa\end{array} \rightleftarrows 2(C_6H_5)_2CONa$$

$$\begin{array}{l}2(C_6H_5)_2CONa + 2(CH_3)_2CHOH \longrightarrow 2(C_6H_5)_2-COH + 2(CH_3)_2CHONa\\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad\downarrow\\ \qquad\qquad\qquad\qquad\qquad\qquad\quad (C_6H_5)_2CO + (C_6H_5)_2CHOH.\end{array}$$

A solution of benzophenone in isopropyl alcohol containing sodium isopropylate becomes greenish-blue on exposure to sunlight, the color being characteristic of the sodium ketyl radical. When the solution is protected from light, the color disappears by the action of the sodium ketyl radical with isopropyl alcohol. Renewed exposure to sunlight restores the color, but when after several days of exposure all of the ketone has been reduced, the solution has again become colorless.

In agreement with the observation of Cohen that Michler's ketone, phenyl-α-naphthyl ketone, fluorenone and 4-phenylbenzophenone are not photochemically reduced to pinacols, Bachmann found that Michler's ketone and phenyl-α-naphthyl ketone could not be reduced to hydrols in this way. Fluorenone underwent a different type of reaction, not photochemical. 4-Phenylbenzophenone, however, was reduced nearly quantitatively to 4-phenylbenzohydrol. In the absence of the alcoholate, it was found to be reduced to the pinacol, 4,4′-diphenylbenzopinacol. Several other substituted ketones behaved in accordance with the new mechanism, yielding hydrols. These included 4-methylbenzophenone, 4,4′-dimethylbenzophenone, 4-methoxybenzophenone, 4-chloro-4′-methoxybenzophenone and 4-chlorobenzophenone. The photochemical reduction process as modified by Bachmann[79] is suitable for the preparation of benzopinacol.

Migita[80] finds that di-*p*-methoxybenzophenone in alcohol is reduced in sunlight to the pinacol.

At 100°C., benzophenone itself undergoes no change when irradiated for nine hours by a mercury arc, and acetophenone none after seven hours.[81] When 0.1 molar solutions in hexane or benzene were irradiated, however, benzopinacol crystallized out with a quantum efficiency of 0.04. None was formed when the solvent was carbon tetrachloride.

According to Jenkins,[82] several ketones of the type $C_6H_5COCH_2C_6H_5$ on standing in light and air undergo autoxidation, yielding acids and aldehydes. Thus $C_6H_5CH_2COC_6H_4Cl$-2 gives benzaldehyde and *o*-chlorobenzoic acid.

Paternò and Chieffi[83] observed on exposing benzophenone and phenylacetic acid in benzene to sunlight for five months that benzopinacol and triphenyllactic acid were formed de Fazi[84] in repeating these experiments always found pressure due to carbon dioxide, on opening the tubes. The reaction of benzophenone with butyric acid also produces carbon dioxide. In the case of the phenylacetic acid reaction, by opening the tube, removing the crystalline deposit of αβ-triphenyl-β-hydroxypropionic acid and benzophenone, and restarting the reaction, successive deposits of this mixture could be obtained. The course of the reaction is believed to be:

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[79] Bachmann, W. E., *Organic Syntheses*, New York, John Wiley & Sons, Inc., **14**, 8 (1934).

[80] Migita, M., *Bull Chem. Soc. Japan*, **7**, 334 (1932); *Chem. Abs.*, **27**, 716 (1933).

[81] Bowen, E. J., and de la Praudière, E., *J. Chem Soc.*, 1503 (**1934**).

[82] Jenkins, S S., *J. Am. Chem. Soc.*, **57**, 2733 (1933).

[83] Paternò, E., and Chieffi, G , *Gazz. chim. ital*, **40**, II, 321 (1910); *Chem. Abs*, **5**, 2632 (1911).

[84] de Fazi, R., *Atti accad. Lincei*, **6**, 266 (1925); *Chem Abs.*, **20**, 594 (1926); *Gazz. chim ital.*, **57**, 551 (1927); *Atti II congr. naz. chim. pura applicata*, 1287 (**1926**); *Chem Abs.*, **22**, 2154 (1928).

$$(C_6H_5)_2CO + C_6H_5CH_2COOH \longrightarrow (C_6H_5)_2C(OH)\cdot CH(C_6H_5)\cdot COOH$$
$$2C_6H_5CH_2COOH \longrightarrow C_6H_5CH_2CH_2C_6H_5 + 2CO_2 + H_2$$
$$2(C_6H_5)_2CO + H_2 \longrightarrow (C_6H_5)_2C(OH)\cdot C(C_6H_5)_2OH.$$

The ability of benzylphenylacetate to react with benzophenone was believed to account for the fact that only a small amount of this compound could be isolated. Irradiation of a similar mixture of phenylacetic acid, benzophenone and benzene in a quartz tube by a mercury arc for 100 hours gave no triphenyllactic acid and only traces of carbon dioxide. Irradiation with a 2000 C.P. Osram lamp, however, produced abundant quantities of these substances. Exposure of phenylacetic acid alone in benzene to sunlight for six months gave little carbon dioxide and a little of a yellow oil. The Osram lamp gave detectable quantities of carbon dioxide in 24 hours. After 280 hours, there were fairly large quantities of gas and some crystals, probably of *s*-diphenylethane.

4,4′-Tetrachlorodimethylbenzophenone is very sensitive to light and is transformed by it into a plastic mass.[85] A similar behavior was observed in the case of 4,4′-di(hydroxymethyl)benzophenone. The *N*-alkyloximes of benzophenone also resinify and decompose rapidly in ultraviolet light.[86] *β*-*o*-Nitrophenylethylketone loses a molecule of water on irradiation and gives a substance with acidic properties, which melts about 300°C.[87]

After a week in direct sunlight in a sealed glass tube, an alcoholic solution of *o*-benzophenonecarboxylic acid yielded the dilactone of tetraphenyldihydroxyethanedicarboxylic acid. Similar reactions were given by *p*-tolyl-*o*-benzoic acid and acetophenone-*o*-carboxylic acid.[88] Straus, Muffat and Heitz[89] noted a reaction whereby 1-phenylpyrazolines are obtained by the action of phenylhydrazine on certain aromatic ketones, owing to the extraordinary ease with which the hydrazones first formed rearrange.

From an investigation of diketones, Porter, Ramsperger and Steel[90] find that under the influence of ultraviolet radiation, benzil in the vapor state is decomposed into carbon monoxide and benzophenone when the temperature is 200°C. or more. In dilute alcohol, in the absence of air, it is partly hydrolyzed to benzoic acid and benzaldehyde, but a portion of it is reduced by the alcohol to benzoin. In aqueous alcohol in contact with air, it is converted into benzoic acid. Further oxidation of the latter gives some salicylic acid.

Benzilic acid is not formed in solutions of benzil. The decomposition products of benzilic acid, namely, benzopinacol in the absence of oxygen, and benzophenone and benzopinacol in its presence, were never found in the exposed benzil solutions. Marchlewski and Wyrobek[91] find benzil to absorb strongly with a maximum at 2590A.

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[85] Connerade, E., *Bull. soc. chim. Belg.*, **43**, 447 (1934); *Chem. Abs.*, **29**, 768 (1935); *Bull. soc. chim Belg.*, **42**, 311 (1933); *Chem. Abs.*, **27**, 507 (1933).

[86] Martynoff, M., *Ann. chim.*, 7, 424 (1937); *Chem. Abs.*, 31, 4973 (1937). For anisalacetophenone, see Stobbe, H., and Hensel, A., *Ber.*, **59**, 2254 (1926).

[87] Tănăsescu, I., and Tănăsescu, E., *Bull. soc. chim.*, **3**, 865 (1936).

[88] Limaye, D. B., *J. Univ. Bombay*, **1**, Pt. 2, 52 (1932); *Chem. Abs.*, **27**, 2097 (1933).

[89] Straus, F., Muffat, C., and Heitz, W., *Ber.*, **51**, 1457 (1918).

[90] Porter, C. W., Ramsperger, H. C., and Steel, C., *J. Am. Chem. Soc.*, **45**, 1827 (1923).

[91] Marchlewski, L., and Wyrobek, O., *Bull. intern. acad. Polonaise*, **93**, **1929A**; *Chem. Abs.*, **23**, 5405 (1929).

PHENOLS

The rays of the quartz mercury lamp, according to Gibbs,[92] color pure phenol light red, in the presence of oxygen, with remarkable rapidity (about one minute). Dermatol (bismuth subgallate) on irradiation produces a violet-colored pigment known as galloflavin.[93] Exposure of 3,4-chloronitrosophenol in ethyl alcohol[94] transforms it into resinous products.

The *m*-cresols are said to color more rapidly on exposure to light and air than the *o*- and *p*-cresols, and gentisic acid and its esters are even more readily colored.[96] Viktorin[97] finds the oxidation of phloroglucinol by atmospheric oxygen to evolve ultraviolet radiations.[98] Schweckendiek[99] finds guaiaconic acid, like guaiaretic acid, to be sensitive to light, the sensitivity being increased by the addition of collodion, Zapon lacquer, or a solution of sulfur in carbon disulfide. The product is green and results from an oxidation process. It may be employed as a photographic process, the green image being fixed with a mixture of ammonium acetate and benzene.

Aside from these scattered observations, little definite seems to be known regarding the photochemistry of the phenols. There is, however, much data on their absorption spectra. Indeed, by measurements in solutions containing various amounts of added alkali, it is possible to determine the dissociation constant of phenol by the changes in its absorption spectrum.[100]

QUINONES

Because of their importance for theories of color, the visible and ultraviolet absorption spectra of the quinones, especially benzoquinone, have been much investigated. This topic, however, lies beyond the scope of this work. Benzoquinone as vapor exhibits a region of fine band absorption from 4800 to 4200A, one of narrow bands between 3100 and 2600A, and a continuous region at shorter wavelengths.[101]

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[92] Gibbs, H. D., *J. Am. Chem. Soc*, **34**, 1193 (1912)

[93] Guyot, R., *Bull. soc. pharm. Bordeaux*, **66**, 18 (1928); *Chem. Abs*, **23**, 4015 (1929).

[94] Hodgson, H., and Kershaw, A., *J. Chem. Soc.*, 1553 (1929). Some data on the effects of various wave-lengths on the oxidation of *d*-catechin in the presence of a complex cobalt salt have been recorded by Shibata and Goda.[95]

[95] Shibata and Goda, *Iwata Inst. Plant Biochem., Publ.* **2**, 175 (1936); *Brit. Chem. Abs.*, **A**, 808 (1936).

[96] Gibbs, H. D., Williams, R. R., and Pratt, D. S., *Philippine J. Sci.*, **7**, 79 (1912).

[97] Viktorin, O., *Chem. Listy*, **29**, 245 (1935); *Brit. Chem. Abs.*, **A**, 7 (1936).

[98] In a method of making photographic prints, the sensitive layer may contain a colorless inorganic oxidizing agent such as nitric acid or lithium nitrate, and a cyclic organic amino- compound such as aminophenol, benzidine, dianisidine, etc. These compounds are sensitive only to ultraviolet light which produces colored compounds. After exposure, the unexposed portions may be washed out with water or other solvent, the colored product being insoluble. British P. 413,093, April 20, 1933, to N. V. Philips' Gloeilampenfabriken. *Brit. Chem. Abs*, **1934B**, 813.

[99] Schweckendiek, C., *Diss.*, Giesen, 1927; *Brit. Chem. Abs.*, **A**, 1041 (1927).

[100] Stenstrom, M, and Goldsmith, N., *J. Phys. Chem.*, **30**, 1683 (1926); Stenström, M., and Reinhard, M., *J. Phys. Chem.*, **29**, 1477 (1925); Job, P., *Compt. rend.*, **186**, 1546 (1928). For other data on the absorption of phenols, see Kepianka, E., and Marchlewski, L., *Bull. soc. chim.*, **35**, 1613 (1924; Valyashko, N. A, *J. Russ. Phys.-Chem. Soc.*, **58**, 779 (1926); *Chem. Abs.*, **22**, 949 (1928); Purvis, J. E., *Proc. Cambridge Phil. Soc.*, **23**, I, 588 (1927); Conrad-Billroth, H., *Z. physik. Chem.*, **20B**, 222, 227 (1933); Savard, J., *Ann. Chim.*, **9**, 287 (1929); **11**, 287 (1929); *Compt. rend.*, **188**, 782 (1929); Lambrechts, A., *Compt rend.*, **198**, 1852 (1934); Kepianka, E., and Marchlewski, L., *Bull. intern. acad Polonaise*, 75, **1926A**; *Bull. soc. chim.*, **39**, 1368 (1926); Goslawski, W., and Marchlewski, L., *Bull Intern. Acad. Polonaise*, 383 **1931A**; de Boer, J. H., and Custers, J. F. H., *Z. physik. Chem.*, **25B**, 238 (1934); Eisenbrand, J., and von Halban, H., *Z. physik. Chem.*, **146**, 30, 101, 111 (1930); Saint Maxen, A., and Dureuil, E., *Compt. rend.*, **197**, 1411 (1933); Marchlewski, L., and Wyrobek, O., *Bull. intern. acad. Polonaise*, 93 **1929A**.

[101] Lifschitz, I., and Rosenbohm, E., *Z. Physik*, **38**, 61 (1926); Light, L., *Z. physik. Chem.*, **122**, 414 (1926).

Benzoquinone in light effects the oxidation of various alcohols. Leighton and Forbes[102] found that when water was also present in large amounts, the reaction exhibited an induction period during which a dimer of the quinone was believed to be formed. When the solvent was 50-per cent alcohol, there was no inhibition. With wave-lengths shorter than 4350A, they found the quantum yield to be 0.5 in alcohol and in aqueous alcoholic solutions. It was independent of the wave-length, and in aqueous alcoholic solutions, also of the concentrations. With longer wave-lengths the quantum yields decreased, indicating the existence of a threshold inside the first absorption band. As the concentration of alcohol was decreased, the threshold was displaced toward shorter wave-lengths. These investigators suggested that every absorbed quantum might produce activation, the observed quantum yields being lowered by a secondary reaction which has an efficiency of but 50 per cent. Recently, these results have been challenged by Berthoud and Porret[103] who observed quantum yields of unity at 4050, 4080 and 4360A. They found the rates to be independent of the quinone concentration and temperature. The rates decrease slowly with decreasing alcohol concentration, and are proportional to the light intensity. Similar results were obtained with isopropyl alcohol.

The oxidation of ferrous sulfate by benzoquinone, but not the reverse process, is sensitive to light. It proceeds with a quantum yield of unity at 4050, 4080 and 4360A and is independent of the temperature and concentrations of reactants.[104]

AROMATIC ACIDS AND THEIR DERIVATIVES

Benzoic Acid. Kailan[105] found ultraviolet irradiation of aqueous solutions of benzoic acid to yield reducing substances, formic acid and oxalic acid. The velocity of the formation of these substances increased as the square of the concentration. Alcoholic solutions are esterfied[106] to the extent of 30 per cent in eight days. The rate is promoted by the presence of a trace of hydrochloric acid

On exposure to acid and sunlight, the esters of the three hydroxybenzoic acids color more rapidly than the free acids; the *meta* compounds are the most rapidly changed; the *para* compounds are practically unaffected[107]

Decomposition of acetylbenzoyl peroxide by ultraviolet light yields carbon dioxide, toluene, methyl benzoate, methane, phenyl benzoate and complex materials of acid and neutral character.[108] Possibly hydrolysis occurs, the necessary water being liberated in the formation of the complex materials.

$$2CH_3COO_2COC_6H_5 + H_2O \longrightarrow C_6H_5COO_2COC_6H_5 + CH_3COOOH + CH_3COOH$$

Fichter and Schnider[109] found the decomposition of dibenzoyl peroxide in ultraviolet light to yield about 80 per cent of the theoretical quantity of carbon dioxide and diphenyl. The residue, an amorphous resin, was not characterized.

Absorption of potassium cyanide by benzaldehyde in the benzoin condensation is unaffected by irradiation.[110] Benzoin, however, is converted into a viscous resin by irradiation, the process being favored by an increase in temperature.

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[102] Leighton, P. A., and Forbes, G. S., *J. Am Chem Soc*, **51,** 3549 (1929); for the actinometric use of benzoquinone, see Chapter 7.

[103] Berthoud, A., and Porret, D, *Helv. Chim Acta,* **17,** 694 (1934)

[104] Porret, D., *Helv. Chim. Acta,* **17,** 703 (1934).

[105] Kailan, A., *Z physik. Chem*, **95,** 215 (1920); *J. Chem. Soc*, **118,** ii, 576 (1920)

[106] Stoermer, R, and Ladewig, H., *Ber.,* **47,** 1803 (1914).

[107] Gibbs, H. D., Williams, R. R., and Pratt, D S, *Philippine J Sci.,* **7,** 79 (1912).

[108] Fichter, F., and Willi, E, *Helv Chim. Acta,* **17,** 1173 (1934).

[109] Fichter, F., and Schnider, A., *Helv. Chim Acta,* **13,** 1428 (1930).

[110] Bousset, R., *Bull. soc. chim.,* **2,** 309 (1935).

Salicylic Acid. Little is known of the photochemical behavior of this acid. Light (but not ultraviolet light) is said to darken the pharmaceutical solutions of sodium salicylate containing sodium bicarbonate. This probably consists in an oxidation with the formation of quinones.[111] Methyl salicylate becomes colored on exposure to air and sunlight, the tint varying from light yellow for short exposures to reddish-brown for protracted ones.[112]

It has been proposed to use such aryl azides as azido-salicylic acid (prepared by the action of sodium azide on diazosalicylic acid) in photographic processes. A layer of the material incorporated in gelatin and exposed under a negative forms a dye, after which the unchanged azide may be washed out.[113]

Of 22 anils known to be phototropic, 15 were said to be derivatives of salicylaldehyde. Recently Brewster and Millam[114] have added three, one a derivative of salicylaldehyde and the other two of 5-bromosalicylaldehyde.

Mandelic Acid. This acid can be oxidized by methylene blue by wavelengths in the range 2540 to 4360A if uranyl nitrate is employed as photosensitizer. In the mechanism suggested by Ghosh, Narayanamurthi and Roy,[115] excited UO_2'' ions yield their energy to mandelic acid, which is decomposed with the production of benzaldehyde, carbon dioxide, water and the UO'' ion. The latter takes an oxygen atom from water, the hydrogen of which reduces methylene blue to the leuco-compound. Oxygen restores the methylene blue, and light excites the uranyl ion so that the processes may be repeated.

Phthalates. When lead phthalate is exposed in a small quartz crucible to ultraviolet rays, the outer layer decomposes rapidly with the formation of a yellowish-brown substance of unknown composition, but probably containing lead oxide. Under the same conditions mercury phthalate is unaffected.[116]

Jaeger[117] claims the decarboxylation of polycarboxylic acids, for example, the conversion of phthalic into benzoic, by subjecting them at 300° to 420°C. in the presence of reducing gases (hydrogen or water gas) to various types of electrical discharge, ultraviolet light, cathode rays or x-rays.

For refining liquid alkyl esters derived from acids produced by the catalytic oxidation of aromatic hydrocarbons, such as dibutyl phthalate, so that distillation of the ester is rendered unnecessary, and its color improved, the material may be exposed to the action of ultraviolet light.[118]

An alcoholic solution of 2,4-dihydroisophthalic acid, which appears to react as a quinone derivative, forms acetaldehyde in sunlight.[119]

Although terephthaldehyde is very stable in the solid state and in solution in benzene in darkness, Suida[120] finds that its solution undergoes rapid atmospheric oxidation when irradiated by a mercury lamp, a white crystalline deposit being formed. This consists of terephthaldehydic acid to the extent of roughly two-thirds, the remainder being terephthalic acid. The solution from which the crystals have separated gives a peroxide reaction with acidified potassium iodide solution.

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[111] Krantz, J. C, Jr., *J Am Pharm. Assoc*, **17**, 1203 (1928); Liberalli, C. H., *Bol. assoc. brasil farm*, **16**, 154 (1935); Chem. Abs., **29**, 5989 (1935)

[112] Stoermer, R., and Ladewig, H., *Ber.*. **47**, 1803 (1914).

[113] British P. 333,820, Nov 3, 1928, to Kalle and Co. *Brit. Chem. Abs.*, **1930B**, 1092.

[114] Brewster, C. M., and Millam, L. H, *J. Am. Chem. Soc.*, **55**, 763 (1933).

[115] Ghosh, J. C., Narayanamurthi, D S., and Roy, N. K., *Z. physik. Chem.*, **29B**, 236 (1935).

[116] Ekeley, J. B., and Banta, C., *J. Am Chem. Soc*, **39**, 762 (1917).

[117] Jaeger, A. O., U. S. P. 1,909,357, May 16, 1933, to Selden Co.; *Brit. Chem. Abs.*, **1934B**, 87.

[118] Smith, F. D., U. S. P. 1,948,281, Feb. 20, 1934 (to Monsanto Chemical Co.); *Chem. Abs.*, **28**, 2725 (1934).

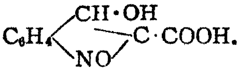
[119] Marzin, A., *J. prakt. Chem.*, **138**, 107 (1933); *Chem. Abs.*, **27**, 5317 (1933).

[120] Suida, H., *Monatsh.*, **33**, 1173 (1912); *J. Chem. Soc.*, **104** (i), 52 (1913).

The oxidation is not accelerated by the presence of nitrobenzene, which, indeed, exerts a hindering effect. A comparison with benzaldehyde seems to indicate that, assuming the supply of oxygen by diffusion to be more than sufficient, the oxidation velocity of each aldehyde group in terephthaldehyde is considerably diminished by the presence of a similar group in the *para* position. Spectrographic examination indicates that the effective rays are those of wave-lengths between 4000 and 3000A, but yellow and red light can cause the oxidation to occur, although only very feebly.

Cinnamic Aldehyde and Cinnamic Acid. These compounds exhibit interesting photochemical reactions because, in addition to the features common to the aldehydes and acids, the presence of a double bond in the side chain offers new possibilities of polymerization and stereoisomerization. Cinnamic acid, in alcoholic solution, exhibits one broad absorption band with a maximum at 2710A. Hydrocinnamic acid, however, in aqueous solution, shows two bands with maxima at 2670 and 2580A.[121]

In sunlight, cinnamic aldehyde reacts with quinone as do other aldehydes. Bargellini and Monti[122] exposed 10.8 gm. of quinone and 13.2 gm. of cinnamic aldehyde in 100 cc. of benzene in a sealed tube for one month. The quinone was reduced to hydroquinone and the aldehyde oxidized to cinnamic acid. These two products then combined, the reaction being analogous to that between phenanthrenequinone and certain aldehydes described by Klinger.[123] According to Stoermer and Ladewig,[124] in the presence of a trace of hydrochloric acid, cinnamic acid reacts with alcohol when irradiated, as much as 37 per cent being esterified in eight days.

When thin layers of finely powdered *o*-nitrocinnamic acid are exposed to sunlight, a red substance melting at 120°C. is produced. It is probably hydroxyisatogenic acid,  $C_6H_4\left\langle\begin{matrix}CH\cdot OH\\ NO\end{matrix}\right\rangle C\cdot COOH$. This is another[125] example of a type of reaction frequently encountered.

The presence of a double bond in the side chain of cinnamic acid permits the existence of *cis* and *trans* forms. Photochemical changes may consist of either a stereoisomerism or a polymerization of either form to a dimer. This, together with the fact that *allo*-(*cis*)-cinnamic acid[125a] is trimorphous, having forms melting at 42°, 58° and 68°C., makes the photochemistry of this compound an intricate subject which has been much investigated, with confusing results. Since the matter is rather highly specialized, space does not permit a complete discussion.[126]

Stoermer[127] showed that ultraviolet light changes the less fusible stable to the more reactive labile forms. The extent of the transformation was thought to be dependent upon the energy differences between the steroisomers. Many derivatives of cinnamic acid were studied[128] and it was believed that in most cases an equilibrium was attained. The number after each of the following compounds represents the percentage of the less fusible form which, at equilibrium, has been transformed: methyl-*o*-nitro-*o*-methoxycinnamate, 80; *p*-methoxycinnamic acid, 25; sodium-*o*-chlorocinnamate, 10; *o*-anisylcinnamic acid, 35-40; *o*-anisylcinnamide, 70; *o*-anisylcinnam-methylamide, 36; and the corresponding ethylamide, 40; β-*o*-anisyl-α-methylcinnamic acid, 5, and the corresponding amide, 5; the form of cinnamic acid melting at 42°C., 30-40. In the case of *o*-chlorocinnamic acid, when glacial acetic acid was employed as solvent, it was observed that, in addition to the expected isomerization, part of the acid combined with the solvent.

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[121] Marchlewski, L., and Wyrobek, O., *Bull. acad. Polonaise*, 331 **(1929)**; *Chem. Abs.*, **24**, 3711 (1930). Ley, H., and Dreinhöfer, R., *Z. wiss. Phot.*, **29**, 134 (1930); Ramart-Lucas and Trivédi, R., *Compt. rend.*, **195**, 783 (1932); Purvis, J. E., *J. Chem. Soc.*, 780 **(1927)**.

[122] Bargellini, G., and Monti, L., *Gazz. chim. ital.*, **60**, 474 (1930); *Chem. Abs*, **25**, 96 (1931).

[123] Klinger, H., *Annalen*, **249**, 137 (1888); **382**, 211 (1911); *Ber.*, **24**, 1340 (1891); **31**, 1214 (1898) In most of this work many of the quinone reactions followed a different course.

[124] Stoermer, R., and Ladewig, H., *Ber.*, **47**, 1803 (1914).

[125] Tănăsescu, I., *Bull soc. chim.*, **41**, 1074 (1927).

[125a] The ordinary *trans*-cinnamic acid melts at 133°C.

[126] de Jong, A. W. K., *Chem. Weekblad*, **26**, 270 (1929) has compiled a large number of references regarding the effects of sunlight on the *cis*- and *trans*-cinnamic acids.

[127] Stoermer, R., *Ber.*, **42**, 4865 (1909); *J. Chem. Soc.*, **8** (ii), 114 (1910).

[128] Stoermer, R., with Frederici, Brautigam and Neckel, *Ber.*, **44**, 637 (1911).

When daylight or sunlight, rather than the light of the mercury arc is used, polymerization reactions also occur with the formation of dimers[129] although isomerization occurs with either sunlight or mercury arc light. Fused *cis*-cinnamic acid is transformed extensively to the *trans* form after 96 hours of mercury arc irradiation. Similarly, α-*trans*-cinnamic acid, fused or in solution, isomerized to the equilibrium mixture. For this change, radiations of wave-length 3200 to 2700A are most effective. The reaction is greatly accelerated by the addition of hydrochloric acid.

When the solid acids or their aqueous suspensions are exposed to sunlight, this change is accompanied by polymerization; α-*trans*-cinnamic acid yields mainly the dimer α-truxillic acid with a little β-truxinic acid. *Allo*-cinnamic acid (*cis*) yields as its polymerization product chiefly β-truxinic acid, together with the isomerization product *trans*-cinnamic acid and its dimer, a little α-truxillic acid. The latter change took place to the extent of 71 per cent after 196 hours in sunlight, but after 200 hours of the mercury arc irradiation only to the extent of 4.4 per cent. Very similar results were recorded for the polymerization of the *trans* acid. Long ultraviolet rays accordingly favor polymerization, but the shorter ones hinder it and exert a depolymerizing action on truxinic and truxillic acids. Each dimer when irradiated by the shorter radiations depolymerizes to the monomer from which it is originally formed by the longer rays.

The metastable β-form of *trans*-cinnamic acid is much more readily isomerized than the stable α-*trans*-cinnamic acid which therefore yields on polymerization but little β-truxinic acid and much α-truxillic acid.

Experiments of this type are further complicated by the fact that some autoxidation to benzaldehyde and in some cases to benzoic acid also occurs. On long illumination of *trans*-cinnamic acid the yield of the dimer, α-truxillic acid, decreases and that of benzaldehyde increases. Analogous results are obtained in the irradiation of *cis*-cinnamic acid.

Stobbe and Zschoch[130] found that the monomeric *trans*-cinnamic acid in 0.0001*N* alcoholic solution absorbs light strongly, although its saturated dimer, α-truxillic acid, is almost completely transparent and begins to absorb only in a 40-mm. layer of a 0.001*N* solution. In a 10-mm. layer of 0.01*N* solutions, its end absorption begins at a wave-length about 600A units shorter than that of the monomer. This difference in absorption accounts for the differing effects of longer and shorter ultraviolet radiations on polymerization and depolymerization. These compounds do not fluoresce.

The quantum yields for the isomerization by the 3130A line have been found to be as follows: Cinnamic acid, 0.003 molar, 0.61; 0.002 molar, 0.53; isocinnamic acid, 0.003 molar, 0.21; 0.002 molar, 0.15.[131]

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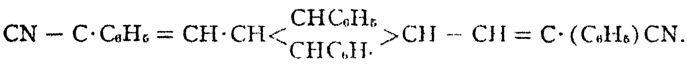
[129] Stobbe, H., *Ber.*, **52B**, 666 (1919); Stobbe, H., and Steinberger, F. K., *Ber.*, **55B**, 2225 (1922). See also de Jong, A. W. K., *Chem. Abs.*, **16**, 2683 (1922); **6**, 2746 (1912); Stoermer, R., and Scholtz, F., *Chem. Abs.*, **15**, 1888 (1921) and Stobbe, H., and Lehfeldt, A., *Ber.*, **58B**, 2415 (1925).

[130] Stobbe, H., and Zschoch, F., *Ber.*, **60B**, 457 (1927).

Various derivatives of cinnamic acid are subject to similar transformations. Stobbe[132] observed methyl *trans*-cinnamate to be converted to a small extent by six months of exposure to sunlight into methyl α-truxillate (2.9 per cent) derived from the solid ester and 0.2 per cent of Liebermann's polyester formed from portions which had been melted by the heat of the sun. The remainder was unchanged. *trans*-Cinnamide was in five months converted into α-truxilldiamide to the extent of 75 per cent. *trans*-Cinnamanilide remains unchanged after six months' exposure in the solid state or suspended in hydrochloric acid. *allo*-Cinnamic anhydride is converted into a mixture of 80 per cent *trans*- and 20 per cent *allo*-anhydride without the production of β-truxinic anhydride, but *trans*-cinnamic anhydride remains unchanged, aside from slight resin formation. Cinnamaldehyde, after eight months in sunlight, yields a mixture of 60 per cent unchanged aldehyde, 33 per cent cinnamic acid and 7 per cent polycinnamaldehyde, apparently a tetramer, which does not yield an oxime or react with ammoniacal silver nitrate or Schiff's reagent. At least 91 per cent of α-bromocinnamic acid remains unchanged after seven months in sunlight or 375 hours in the light of a mercury vapor lamp; the remainder is converted by autoxidation into oxalic acid, benzoic acid and free bromine. No polymerization or resin formation occurred. Gulland and Virden[133] find the yellow *trans*-2-amino acid obtained by the reduction of 3,4,2′,5′-tetramethoxy-2-nitro-*trans*-α-phenylcinnamic acid, in alcoholic solution to give after several days in ultraviolet light, 7,8,2′,5′-tetramethoxy-3-phenylcarbostyril. The action of ultraviolet light on the sodium salt of *trans*-2-nitro-3,4,2′,5′-tetramethoxy-α-phenylcinnamic acid gives a small yield of the *cis* form.

o-Hydroxycinnamic acid is oxidized by peracetic acid in darkness to *cis-cis*-muconic acid in very small amount; in light a more or less complete isomerization to the *trans-trans* acid occurs.[134] *cis-cis*-Muconic acid, in 96 per cent alcohol with a trace of iodine, is almost quantitatively rearranged into the *trans-trans* compound.

Acids containing the cinnamylidene residue and their nitriles have also been extensively investigated. Solutions of α-phenylcinnamylideneacetonitrile in benzene or chloroform in either the presence or absence of iodine in sunlight form two dimers, one melting at 197°C. and the other at 215°C.[135] The former is 1,3-diphenylcyclobutane-2,4-diatroponitrile, also called 1,3-diphenyl-2,4-*bis*-(β-phenyl-β-cyanovinyl)cyclobutane:



$$CN - C\cdot C_6H_5 = CH\cdot CH\begin{matrix}\diagup CHC_6H_5 \diagdown \\ \diagdown CHC_6H_5 \diagup\end{matrix}CH - CH = C\cdot(C_6H_5)CN.$$

The isomerism of the two dimers may be of the *cis-trans* type, depending on a difference of location of the phenyl and cyano- groups at one or both of the double bonds of the side chain, since on treatment with permanganate both yield α-truxillic acid

According to Lohaus,[136] exposure of a solution of the stable ethyl cinnamylidenecyanoacetate in ethyl alcohol in the presence of a little sulfuric acid gives after one day in sunlight a labile form. Further exposure of the crystalline material recovered yields a cyclobutane derivative previously described by Reimer (1911, 1913). In the absence of sulfuric acid, however, the original compound polymerizes to an open-chain dimer, melting at 165°C. The labile form of ethyl cinnamylidene cyanoacetate is rapidly converted into its stable form when its alcoholic solution, containing iodine, is exposed to sunlight in quartz vessels.

allo-(*trans,cis*)-Cinnamylideneacetic acid is converted into the normal (*trans-trans*) form by irradiation of its solutions in the presence of iodine.[137] Equilibrium is attained when 90-per cent conversion has been effected, this equilibrium being independent of the concentration of iodine and the intensity of the light and but little dependent on the temperature. Constant unimolecular rate constants could be obtained when concentrations of iodine greater than 0.024*N* were used, but at lower concentrations the rate constant for the forward reaction showed a gradual increase with time indicative of an induction period. This was observed only when freshly prepared solutions were used. With increasing iodine concentrations the rate constant passed through a maximum. The values of the constants decreased with increasing initial concentrations of the compound. They were proportional to the intensity of the light (5000A). A quantum yield of 423 was found. Green light was most effective, then blue, yellow and red light.[138] The rates were highest in methanol, and decreased in other solvents in the order ethanol, mixtures of ethanol and water, and mixtures of chloroform and methanol. In chloroform the rates were very low in comparison with those in solutions containing the hydroxyl group. For benzene or chloroform as solvents Ghosh, Murthi and Das-Gupta[139] have suggested the following reactions as entering the mechanism, in which A represents the *allo*-acid employed and B the normal acid formed.

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[131] Vaidya, B. M., *Proc. Roy. Soc.*, **A129,** 299 (1930)

[132] Stobbe, H., *Ber.*, **58B,** 2859 (1925); *Chem. Abs.*, **20,** 1612 (1926)

[133] Gulland, J. M., and Virden, C. J., *J. Chem. Soc.*, 1478 (**1928**)

[134] Grundmann, C., and Trischmann, H., *Ber.*, **B69,** 1755 (1936), *Chem. Abs.*, **30,** 6354 (1936)

[135] Stobbe, H., and Kuhrmann, F., *Ber.*, **58B,** 85 (1925); *J. Chem. Soc.*, **128,** I, 253 (1925).

[136] Lohaus, H., *Annalen*, **514,** 137 (1934); *Chem. Abs.*, **29,** 1796 (1935)

[137] Ghosh, J. C., and Mitra, M. N., *J. Indian Chem. Soc.*, **3,** 273 (1926); *Brit. Chem. Abs.*, **1927A,** 560.

$$
\begin{aligned}
&I_2 + h\nu \longrightarrow I + I \\
&I + A \longrightarrow IA \\
&IA \longrightarrow I + B \\
&I + B \longrightarrow IB \\
&IB + A \longrightarrow I + B + B.
\end{aligned}
$$

They also find that the rate constant increases with the light intensity, at first rapidly and then more slowly; it also varies with the square root of the energy absorbed.

Vorländer and Gieseler[140] find that exposure of a solution of the sodium salt of *trans-trans-p*-methoxycinnamylideneacetic acid to ultraviolet light causes the formation of salts of two acids (or mixtures of acids), melting at 90-96° and 106-110°C., respectively. Both of these regenerate the original acid when their benzene solutions with iodine are exposed to sunlight Under these conditions, *allo-p*-methoxycinnamylideneacetic acid is converted into the *trans-trans* form. Cinnamylidene-*m*-nitroacetophenone yields, in 10-per cent chloroform solution after 15 days in sunlight or 12 hours in ultraviolet from a mercury lamp, a semisolid substance which slowly forms a resin with a fracture like that of colophony.[141] In this resinification, it differs from cinnamylideneacetophenone, which polymerizes under the action of light.[142]

The ability of dicinnamalacetone to form insoluble, noncrystalline products on exposure to light when exposed in a layer with shellac and a basic dye has led Seymour[143] to propose its use in photographically printing dyed relief images.[144]

The photochemical addition of bromine to α phenylcinnamonitrile[145] under conditions of slight absorption of light proceeds at a rate proportional to the square root of the intensity and to the 1.5 power of the bromine concentration. Under conditions of total absorption, it is proportional to the square root of the intensity and to the bromine concentration. The temperature coefficient is 1.4. The dibromide, once formed, can also be photochemically decomposed in the presence of bromine, which acts as a sensitizer. The rate is retarded by the presence of a large excess of the nitrile.

Halogenation of Cinnamic Acid. The rate of photobromination of cinnamic acid is dependent upon the form of the acid employed. The thermal rate for *allo*-cinnamic acid, melting at 68°C., is increased five-fold by yellow light, but that of the ordinary acid (melting 133°C.) is increased forty-fold.[146] In darkness, the rate of bromination of the *allo*-acid melting at 58°C. is greater than that of the form melting at 68°, but the form melting at 42°C. is more rapidly brominated than either of these. These differences led Meyer and Pukall to regard the three forms of the *allo*-acid as isomers, unexplained by ordinary stereochemical concepts, rather than as polymorphs. They were unable to obtain constant rate values by the use of yellow, blue or yellowish white light and the 133°C. ordinary cinnamic acid, but with red or green light found the reaction to be bimolecular.

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[138] Ghosh, J. C., Das Gupta, D. N., Roy, N C, and Chatterjee, H. K., *J. Phys. Chem.*, **34**, 2771 (1930).

[139] Ghosh, J. C, Murthi, D. S. N, and Das Gupta, D N, *Z. physik. Chem.*, **B26**, 255, 267 (1934).

[140] Vorlander, D., and Gieseler, K, *J prakt. Chem.*, **121**, 247 (1929); *Chem. Abs.*, **23**, 3912 (1929).

[141] Giua, M., *Gazz. chim. ital.*, **55**, 567 (1925); *Chem Abs.*, **20**, 749 (1926).

[142] Stobbe, H., and Rücker, C., *Ber.*, **44**, 869 (1911); *Chem. Abs.*, **5**, 2253 (1911).

[143] Seymour, M. W., U. S. P. 2,063,348, Dec. 8, 1936, to Eastman Kodak Co.; *Chem. Abs.*, **31**, 621 (1937).

[144] For a study of the photodimers of cinnamalmalonic acid, see Stobbe, H., Hensel, A., and Simon, W., *J. prakt. Chem.*, **110**, 129 (1925).

[145] Berthoud, A., and Nicolet, G., *Helv. Chim Acta*, **10**, 417 (1927); *J. chim. phys.*, **25**, 40 (1928).

[146] Meyer, J., and Pukall, W., *Z. physik. Chem.*, **A145**, 360 (1929); see also Padoa, M., and Vita, N., *Gazz. chim. ital*, **58**, 3 (1928).

Yajnik and Uppal[147] found that, for equimolar concentrations of bromine and cinnamic acid in either carbon disulfide, carbon tetrachloride or chloroform, the formula for unimolecular reactions gave sufficiently constant values for the rate constant. A temperature coefficient of 2.8, increasing with the wave-length used, was observed by Ghosh and Purkayastha,[148] who found the velocity coefficient independent of the concentration of bromine. It increased with the initial concentration of the cinnamic acid and varied as the square root of the intensity of incident blue light. For green light, the increase was greater. They found that there was an induction period and an after-effect, from which they assumed the existence of a complex intermediate. Excited bromine molecules were considered to function in the mechanism. One quantum of light was observed to form 426 molecules of dibromophenylpropionic acid in one experiment. Other values were, in carbon tetrachloride, 22 at 5330A and 43 at 4880A, and in carbon disulfide, 101 and 156, respectively. Berthoud and Béraneck[149] believed the velocity in carbon tetrachloride to be affected by an unknown catalyst, the effect of which they could not completely eliminate. They differed from the Indian workers in finding the reaction independent of the concentration of acceptors, such as cinnamic acid. With strong absorption, it was nearly first order with respect to bromine, but with weak absorption, it was of 3/2 order. The quantum yield was about 36 with a violet filter and 10 with a green filter. Rotating sectors, transmitting 50 and 25 per cent of the light, reduced the velocity to 65 and 43 per cent. This use of sectors has been criticized by the Indian workers. The mechanism of Berthoud assumes that bromine atoms participate in reaction chains.

$$
\begin{aligned}
A + Br &\longrightarrow ABr.\\
ABr + Br_2 &\longrightarrow ABr_2 + Br.
\end{aligned}
$$

Ghosh, Bhattacharya and Murthi[150] find the combined effect of any two radiations selected from 546, 436 and 406 mμ to be less than the sum of the two separate effects.

Bauer and Daniels[151] confirmed the chain nature of the reaction but found much lower quantum yields, 1 to 15 or more, varying with the concentration of the bromine and the temperature. The yields decrease linearly with dilution to unity at infinite dilution. The nature of the reaction was thought to be complex since, in addition to the primary process with a quantum yield of unity, it involved also a photo-excited thermal reaction which can be suppressed by the use of low bromine concentrations and low temperatures. They believed that this reaction forms an example of an energy chain carried by activated bromine molecules.

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[147] Yajnik, N. A., and Uppal, H. L., *J. Indian Chem. Soc.*, **6**, 729 (1929); *Brit. Chem Abs.*, **1930A**, 174. See also Mathur, K. G., Gupta, R. S., and Bhatnagar, S. S., *Indian J. Physics*, **2**, 243 (1928) and Berthoud, A., *J. chim. phys.*, **26**, 435 (1929).

[148] Ghosh, J. C., and Purkayastha, R. M., *J. Indian Chem. Soc.*, **2**, 261 (1925); *Chem. Abs.*, **20**, 1953 (1926); *Quart. J. Indian Chem. Soc.*, **4**, 409, 553 (1927); *Brit. Chem. Abs.*, **1928A**, 172, 256.

[149] Berthoud A., and Béraneck, J., *J. chim. phys.* **24**, 213 (1927); *Helv. Chim Acta*, **10**, 289 (1927).

[150] Ghosh, J. C., Bhattacharya, S. K., and Murthi, M. L. N., *J. Indian Chem. Soc.*, **14**, 452 (1937); *Chem. Abs.*, **32**, 4881 (1938).

[151] Bauer, W. H., and Daniels, F., *J. Am. Chem. Soc.*, **56**, 378 (1934); **56**, 2014, 2564 (1934); see also Ghosh and Purkayastha, *J. Indian Chem. Soc.*, 235 **(1933)**, and Ogg, R. A., Jr., *J. Am. Chem. Soc.*, **58**, 607 (1936).

In ether in diffuse sunlight at −10°, cinnamic aldehyde adds the theoretical amount of bromine, but in brighter light, substitution also occurs. *trans*-Cinnamic acid in sunlight added practically the theoretical amount.[152] *m*-Methoxycinnamic acid in boiling carbon tetrachloride gave α,β-dibromo-β, 3-methoxyphenylpropionic acid. In darkness in acetic acid, there is a quantitative yield of the 6-brom-derivative of the cinnamic acid and this is also formed in boiling acetic acid in sunlight. In boiling chloroform, a mixture of the two products forms. Analogous results are found with the ethyl ester in these solvents. 6-Brom-derivatives of the methoxycinnamic acid, on bromination in carbon tetrachloride in sunlight give the β-6-bromo-derivative of the propionic acid. α-Bromo-*m*-methoxy-*allo*-cinnamic acid is transformed into α-bromo-*m*-methoxycinnamic acid (the *trans* form) by sunlight.

For the chlorination of cinnamic acid, Basu[153] found, in carbon tetrachloride exposed to the full radiation from a quartz lamp, at 22.6°C., a unimolecular rate constant of 3.8×10^{3}, with respect to chlorine. It was unaffected by changes in the cinnamic acid concentrations. In darkness, there was a constant of 4×10^{-5}. At the wave-lengths 3665, 4040 and 4360A, the quantum yields were 7, 4, and 2. Since no fluorescence could be observed, Basu proposed a mechanism involving, of the chlorine atoms produced in the primary process, only the excited ones as carriers of the chains. The chain length was thought to depend upon the amount of energy associated with the intermediary monochloride of cinnamic acid. Berthoud and Porret[154] believed this reaction to follow the same laws as the photobromination. The life of a reaction chain was considered to be less than 0.02 second. The quantum yields varied with the experimental conditions, being 2.4 in one case. The rate was independent of the concentration of acid, and proportional to the chlorine concentration for total absorption, or to the two-thirds power for weak absorption. It was also proportional to the square root of the light intensity.

Woods and Poulter[155] believed they had demonstrated the ability of ultraviolet light to alter slightly the polarity of the double bond in cinnamic acid. When its solution in absolute ether was irradiated for an hour with the highly polar reagent hydrogen bromide, the residue after evaporation of the ether yielded to ligroin a small portion of material which on recovery from the solvent melted at about 50°C. and had physical properties very similar to those of the compound $C_6H_5CH_2$-CHBrCOOH.[156]

Coumarin, the inner lactone of *o*-hydroxycinnamic acid, also possesses a double bond and is subject to reactions analagous to those of cinnamic acid. It exhibits two absorption maxima at 3200 and 3600A[157] but when one or two hydroxyl groups are introduced into the benzene ring, the resulting products show only one absorption maximum. It has been found that when certain immature plants, which when mature contain coumarin, are irradiated by a mercury-vapor lamp, the odor of coumarin becomes perceptible in a few minutes.[158]

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[152] Duquenois, P., *Bull soc. chim.*, **4**, 193 (1937).

[153] Basu, K. P., *J. Indian Chem. Soc.*, **6**, 341 (1929); *Chem. Abs.*, **24**, 784 (1930)

[154] Berthoud, A., and Porret, D., *Helv. Chim. Acta*, **17**, 237 (1934).

[155] Woods, G. M., and Poulter, T. C., *Proc. Iowa Acad. Sci.*, **35**, 217 (1928); *Chem. Abs.*, **24**, 1101 (1930).

[156] For data on the photobromination of α-phenylcinnamic acid, see Berthoud, A., and Porret, D., *Helv. Chim. Acta*, **17**, 1548 (1934).

[157] Tasaki, T., *Acta. Phytochim*, **3**, 21 (1927); *Chem. Abs.*, **22**, 1543 (1928).

[158] Pougnet, J., *Compt. rend.*, **151**, 355, 566 (1910).

The photobromination of coumarin attains an equilibrium similar to that described by Berthoud and Nicolet for phenylcinnamonitrile. The rate of bromination is greater in carbon tetrachloride than in chloroform, but the reverse is true of the thermal reaction. Williams[159] finds that in ultraviolet light and with 60 molar concentrations of coumarin and bromine, an equilibrium results in 25 minutes in carbon tetrachloride at which time 85.6 per cent of the bromine had reacted. In chloroform, 65.8 per cent had reacted at equilibrium, reached in 45 minutes.

Considerable work has been done on the geometrical photoisomerizations of coumarin and its derivatives. Although Perkin had noted the conversion of methylcoumarinic acid into methylcoumaric acid by sunlight, Stoermer[160] found the tendency the other way in the coumaric acid series, the stable form changing to the labile in ultraviolet rays. Coumaric acid yields 75 per cent of coumarin, and methylcoumaric acid yields 75 per cent of methylcoumarinic acid, while ethylcoumaric acid and acetylcoumaric acid are quantitatively changed to the corresponding coumarinic acids. Benzene or alcoholic solutions were used. Vaidya[161] found the following quantum yields (3130A) for the transformation of coumaric acid: 0.005 molar, 0.031; 0.002 molar, 0.023.

Dey, Rao and Seshadri[162] have pointed out that the esters undergo inversion more readily than the acids. The presence of a nitro- group in the benzene ring accelerates the transformation of both acids and esters but a methoxyl group has the opposite effect. An alcoholic solution of *o*-coumaric acid formed coumarin in 48-per cent yield after six hours of exposure to light and 65-per cent after 24 hours. The methyl and ethyl esters underwent 87- and 74 per cent conversion in 24 hours. Ordinary sunlight supplies the requisite energy for the transformation of the *trans* forms of the coumaric acids and their esters into the *cis* form with higher energy content.

OTHER AROMATIC COMPOUNDS WITH DOUBLE BONDS IN A SIDE CHAIN

Styrenes. Smakula[163] measured the absorption spectra of a number of polystyrenes of molecular weights 3,900 to 240,000. All showed an absorption band at 2600A, the intensity of which increased directly with the molecular weight. A comparison of their spectra with those of styrene and of ethylbenzene showed that the absorption bands belong to the phenyl radicals.

Obviously, stereoisomeric forms of styrene, phenylethylene, cannot exist because of the symmetry of the CH_2. The possibility of photoreaction is therefore limited to polymerization. Stobbe[164] found that an equilibrium is set up between styrene and metastyrene. Styrene solution (5 per cent) showed the following changes in refractive index after 0, 20, 32, 95 and 230 hours of irradiation in Uviol tubes: 1.49883, 1.49911, 1.49939, 1.4994, 1.4994. Metastyrene showed the values: 1.50125, 1.50125, 1.50125, 1.50116, 1.50116. The irradiated solution of styrene gave a precipitate of metastyrene with alcohol: that of metastyrene decolorized permanganate, but the solutions kept in darkness did not.

Taylor and Vernon[165] found the photopolymerization could be accelerated by previous storage of the styrene in contact with oxygen. After 144 hours in contact with hydrogen, styrene polymerized when irradiated in Pyrex at a rate of 5.85 per cent per hour. When stored with oxygen, the rates were at the start, 6.39 per cent; 48 hours, 9.14 per cent; 96 hours, 9.15 per cent and 144 hours, 10.25 per cent per hour. Over oxygen, however, there is both oxidation as well as polymerization. To obtain the true rate of polymerization, hydrogen-distilled samples must be used. The temperature coefficient of polymerization is 1.33 per 10° between 30° and 70° and slightly less, 1.27, between 70° and 100°C. From viscosity measurements it seems that the aggregates formed at higher temperatures were of much larger size than those formed at low temperatures. Quantum yields of 4 at 3000 to 4000A and 7.4 at 2536A indicate a chain mechanism. Hydroquinone inhibits the change, partly by internal filtering and partly by deactivating collisions.

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[159] Williams, D. M., *J. Chem. Soc.*. 1383 (1929).

[160] Stoermer, R., *Ber.*, **42**, 4865 (1909); **44**, 637 (1911); *J. Chem. Soc.*, **98**, II, 114 (1910)

[161] Vaidya, B. M., *Proc. Roy. Soc*, **A129**, 299 (1930).

[162] Dey, B. B., Rao, R. H. R., and Seshadri, T R, *J Indian Chem. Soc.*, **11**, 743 (1934); **12**, 140 (1935); *Chem. Abs.*, **29**, 4752 (1935).

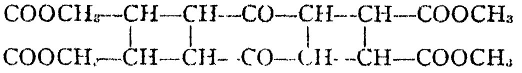
[163] Smakula, A., *Angew. Chem.*, **47**, 777 (1934).

[164] Stobbe, H., *Ber.*, **47**, 2701 (1914).

[165] Taylor, H. S., and Vernon, A. A., *J. Am. Chem. Soc.*, **53**, 2527 (1931).

A low-boiling form of nitro-ω-bromostyrene, in which stereoisomerism is possible, is converted into a high boiling form by exposure to ultraviolet light.[166]

bis-Distyrylketone is, according to Stobbe, Farber and Rau,[167] readily depolymerized to distyrylketone in the light of a mercury vapor lamp. Di-*p*-methoxystyrylketone is polymerized, but its addition compounds with uranyl chloride or stannic chloride do not appear to yield a dimer when exposed to light. Methyl-γ-ketopentadienedicarboxylate



$$\begin{array}{l} COOCH_3-\overset{}{CH}-CH-CO-CH-CH-COOCH_3 \\ \qquad\qquad\ \ | \qquad\ \ | \qquad\qquad\ \ | \qquad\ \ | \\ COOCH_3-CH-CH-CO-CH-CH-COOCH_3 \end{array}$$

is readily converted by light into a dimer not oxidized by permanganate and not capable of decolorizing bromine Under analogous conditions, ethyl γ-ketopentadienedicarboxylate appears to suffer deep oxidative fission.

Exposure of an alcoholic solution of the yellow form of 2-hydroxystyrylmethyl ketone to rays of short wave-length from a quartz mercury vapor lamp for 24 hours produces a complete transformation to the colorless form.[168]

Derivatives of benzoylethylene also exhibit geometrical isomerizations. *Trans-α,β-bis*(2,4-dimethylbenzoyl)ethylene, on exposure to light, becomes coated with the *cis* isomer, which appears to revert slowly to the *trans* form on recrystallization.[169] α-Chlorodibenzoylethylene is transformed into the β-isomer by exposing a chloroform solution containing a trace of dibenzoyl-α,β-dichloroethane to strong sunlight for two hours Dibenzoylbromoethylene is not, however, changed by sun light. Dibenzoyldichloroethylene exists in two forms: α, melting at 63-65°C. is more soluble in chloroform than the β-form, melting at 162°C. The former is transformed into the latter by strong sunlight. Similar transformation occurs also in the case of the dibromo-derivative.[170] Sunlight also isomerizes the yellow benzoylethylene phenyl sulfone, as well as β-bromo-β-benzoylvinyl phenyl sulfone, to colorless isomers with altered melting points.[171]

Von Halban and Geigel [172] have shown that, in the case of tetrabenzoylethylene, an irreversible chemical change rapidly follows a primary phototropic process. Von Halban and Rast [173] state that when it is dissolved in acetic acid, concentrated sulfuric acid or sodium ethylate, a monohydrate can be crystallized out. On further illumination, a colorless powder, melting at 300°C., very slightly soluble and of unknown molecular weight is obtained, apparently as the result of an internal oxidation. The corresponding reduction product can not, however, be obtained. In indifferent solvents, a yellow substance is formed. The quantum yields for the conversion of *cis-* into *trans*-stilbene in hexane solutions by various mercury lines are, according to Smakula,[174] 3130A, 1.01; 3020A, 0.73; 2650A, 0.73; 2260A, 0.41; 1930A, 0.36.

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[166] Dann, A. T., Howard, A., and Davies, W., *J Chem. Soc.*, 607 (1928).

[167] Stobbe, H., Färber, E., and Rau, F., *Ber*, **58B**, 1548 (1925).

[168] McGookin, A, and Heilbron, I M., *J. Chem. Soc*, **125**, 2102 (1924).

[169] Coulson, E. A., *J Chem. Soc.*, 1406 (1934).

[170] Conant, J. B., and Lutz, R. E., *J. Am Chem Soc.*, **47**, 881 (1925)

[171] Kohler, E. P., and Larsen, R. G., *J. Am. Chem. Soc.*, **57**, 1448 (1935).

[172] von Halban, H., and Geigel, H, *Z. physik. Chem.*, **96**, 233 (1920).

[173] von Halban, H., and Rast, K., *Z. physik. Chem.*, *Bodenstein-Festband*, 303 (1931).

Mercury arc irradiation of biphenylenethylene in ether completes its polymerization in two hours. The polymer when heated at 300-330° gives fluorene, methylfluorene, and a small quantity of a yellow hydrocarbon, $C_{27}H_{10}$, with blue fluorescence in benzene.[175]

Chalcone. The condensation product of benzaldehyde and acetophenone, benzylideneacetophenone, is known as chalcone. On irradiation, it forms two dimers.[176] The dimer A, melting at 124°C. (truxinic ketone type) undergoes some decomposition (probably a depolymerization) with production of brown resins, when irradiated by sunlight or the mercury arc either as solid or in solution. The other dimer, B, (truxillic ketone type) is decomposed only to a slight extent by irradiation in the solid state or in chloroform solution.

Irradiation of chalcone in solution gives the dimer A only, the yields being about 30 to 35 per cent in the solvents acetic acid, chloroform, or ethanol. Less is formed in benzene solution. The yield is not affected by the presence or absence of oxygen, or hydrochloric acid or of erythrosine. In the presence of chlorophyll, however, the yield is cut to one-third its usual value and 1 to 1.5 per cent of dimer B is also formed.

Still a third dimer, C, was obtained to the extent of 7.5 per cent in one experiment in which a benzene solution was irradiated by a quartz mercury arc. Irradiation in the solid state or in suspension produces both the dimers A and B, the yield of the latter decreasing with the use of progressively shorter wave-lengths.

The results are to be compared with those of cinnamic acid and of the methyl esters of benzalpyruvic acid. With chalcone in solution, there is polymerization rather than isomerization, but the cinnamic acids in solution isomerize rather than polymerize. The production of the lower melting truxinic ketone type of dimer from chalcone in solution and of the higher melting truxillic ketone type in the solid state process agrees with the behavior of the benzalpyruvate esters.

The absorption spectra of chalcone, dihydrochalcone and the dimers conform to the general rule[177] that the curves of dimers lie between those of the monomer and of the saturated dihydro- compound. Stobbe and Bremer also reported data on various methyl and methoxy chalcones. In general, it was found that unsubstituted chalcone and all *p*- or *p'*-monosubstituted chalcones tended to polymerize in light. On the other hand, *pp'*-disubstituted ones resisted this process and in most instances exhibited a great tendency to resinification. Solid 3,4-methylenedioxychalcone was apparently unaffected.

No general relation between light-sensitivity and constitution could be found between the various chalcones and the corresponding cinnamic acids. Chalcones with an α-substituted ethylene, ArCH=CR—COAr, readily isomerize when R is a methyl or phenyl group, but not when it is an acetyl or $COOC_2H_5$. In neither case did polymerization occur. The only β-substituted chalcone examined (dypnone or β-methylchalcone) was unaffected by ultraviolet light when exposed alone or in solution. In the similarly constituted cinnamic acids, either α- or β-substitution generally hinders polymerization, although exceptions are known.

Exposure of the anti- oxime of chalcone to ultraviolet light produced a certain amount of discoloration but no polymerization. The α-semicarbazone, which melts at 168°C., yielded equal quantities of resin and unchanged product, but the form with melting point between 179° and 180°C. readily underwent a peculiar transformation to a yellow isomer.[178] It was shown later by Stobbe and Bremer[179] that both the α- and γ-chalcone semicarbazones, which are stable in darkness, become yellow when exposed to ultraviolet light, the change occurring readily in diffuse daylight in the case of the γ-compound. In alcohol or chloroform, both yellow forms give colorless solutions. These on concentration in darkness yield the colorless form, but in light the yellow form. The colorless forms give yellow solutions in alcoholic sodium alkoxide, sodium hydroxide or piperidine, acidification restoring the colorless form. They suggest that the yellow color in sodium alkoxide solution is not due to stereoisomerism as had been suggested by Heilbron and Wilson, but to salt formation within the urea portion of the molecule.

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[174] Smakula, A., *Z. physik. Chem.* **25B**, 90 (1934).

[175] Wieland, H. and Probst, O., *Annalen*, **530**, 274 (1937).

[176] Stobbe, H., and Hensel, A., *Ber.*, **59**, 2254 (1926); Stobbe, H., and Bremer, K., *J. prakt. Chem.*, **123**, 1 (1929); *Chem. Abs.*, **24**, 92 (1930); *Brit. Chem. Abs.*, **1930A**, 1180.

[177] Stobbe, H., *Z. angew. Chem.*, **39**, 673 (1926). For studies on o-nitrochalcones, see Tănăsescu, I., and Baciu, A., *Bull. soc. chim.*, **4**, 1742 (1937).

[178] See also Heilbron, I. M., and Wilson, F. J., *J. Chem. Soc.*, **101**, 1482 (1912).

[179] Stobbe, H., and Bremer, K., *J. prakt. Chem.*, **123**, 241 (1929).

$R:N.NH.CO.NH_2 \longrightarrow R:NNH.C(OH):NH$ or $R:N.N:C(OH).NH_2$ in which R is $CHC_6H_5:CH.CC_6H_5:$. Similarly, the yellow forms obtained on exposure of the colorless semicarbazone are equilibrium mixtures of the keto-form with the *aci*-forms.

It was found that in general, the γ-forms of substituted chalcone semicarbazones are less light-stable than the α-forms and become colored in diffuse daylight. Both forms are colored by fifteen minutes of exposure to ultraviolet light. Comparison with the semicarbazone of 4′-methyldihydrochalcone and other saturated aromatic and aliphatic ketones and with various arylideneacetones showed that only the derivatives of unsaturated ketones become colored on exposure to ultraviolet light, or give colored solutions in sodium ethoxide, or enol tests with ferric chloride. The tautomeric change is therefore believed to be dependent upon the presence of conjugated double linkings.

Methyl benzalpyruvate, on exposure in dry form to sunlight, gives a small quantity of a polymeric ester, melting at 154°C. and an oil, which may be a mixture of isomers and decomposition products. In benzene solution there was also formed, as previously noted, a polymer melting at 117°C. The behavior of the higher-melting polymer led Reimer[180] to assign it a structure of the truxillic acid series, the lower-melting form being assigned to the truxinic acids. The formation of the latter was explained by assuming, as in the case of the cinnamic acids, that in solution isomerization first occurred, the product polymerizing. It was pointed out that it is unusual for polymerization of this type of substance to occur in solution, although a few cases had been described.[181]

It was found by Rice[182] that the yellow methyl and ethyl esters of benzoylacrylic acids are transformed in sunlight into the corresponding colorless stereoisomeric esters. The reverse transformation takes place when solutions containing a trace of iodine or bromine are exposed to sunlight. The *p*-methoxybenzoyl (and ethoxy) acrylic esters behave similarly.

Bogert and Ritter[183] stated that β-benzoylacrylic acid is not isomerized by ultraviolet light, but Rice later states[184] that methyl *p*-phenoxybenzoylacrylate is changed in benzene solution by sunlight from the stable yellow form to the labile, colorless isomer. The reverse change is effected by the addition of a trace of iodine to the benzene solution. When the yellow modification is exposed as a thin layer of solid, it is rapidly converted to a colorless polymer, $C_{31}H_{28}O_8$. Rice, however, agrees that free *p*-phenoxybenzoylacrylic acid is not changed by sunlight in benzene solution. In cool weather, it is also unchanged when exposed as a solid, but in hot weather it becomes coated with a carrot-colored layer. She also shows that sunlight transforms the yellow form of methyl bromo-5-bromo-2,4-dimethoxybenzoylacrylate into the colorless form.[185] da Costa[186] obtained *cis*-α-methyl-β-anisylacrylic acid and *cis*-β-methyl-β-anisylacrylic acid by irradiation of aqueous solutions of the sodium salts of the corresponding *trans*-acids.

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[180] Reimer, M., *J. Am. Chem. Soc.*, **46**, 783 (1924).

[181] Ciamician, G., and Silber, P., *Ber.*, **42**, 1388 (1909); Stobbe, H., and Rücker, C., *Ber.*, **44**, 869 (1911); Reimer, M., and Keller, E., *Am. Chem J.*, **50**, 157 (1913).

[182] Rice, G. P., *J. Am. Chem. Soc*, **45**, 222 (1923); **46**, 214, 2319 (1924).

[183] Bogert, M. T., and Ritter, J. J., *J. Am. Chem. Soc.*, **47**, 526 (1925).

[184] Rice, G. P., *J. Am. Chem. Soc.*, **48**, 269 (1926).

[185] Rice, G. P., *J. Am. Chem. Soc.*, **50**, 1481 (1928).

[186] da Costa, R. M., *Compt. rend.*, **198**, 1996 (1934).

Reimer[187] discussed the difference in behavior of the benzalpyruvates and th benzoylacrylic acids just described.

$C_6H_5CH{=}CHCOCOOR$	$C_6H_5COCH{=}CHCOOR$
Benzalpyruvates	*Benzoylacrylates*

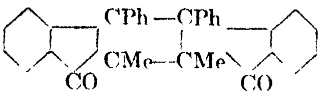
The system of conjugated double bonds is the same in each case, but its relatio to the phenyl and carboxyl groups differs. The representatives of the first polymerize but those of the second isomerize instead. Miss Reimer later found[18 that benzalpyruvic acids in which methoxyl groups are substituted in the nucleu are less affected by sunlight. The most active substance is colorless β-bromobenzalpyruvic acid.[189] Its benzene solutions become lemon-yellow in two o three days in diffused light. Direct sunlight fades this to colorless, the colo reappearing after removal from sunlight. The color change can be repeated man times and is remarkably sensitive to changes in intensity. From the decolorize solutions, a white crystalline dimer was isolated. It became brilliantly yellow overnight. The yellow form is regarded as a geometrical isomer of the origina acid.

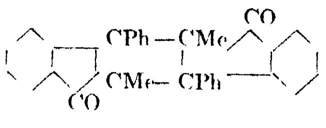
In stoppered tubes, there is also a photodecomposition of some of the compounds producing hydrogen bromide. The yellow form and the polymer are no obtained, but brown decomposition products result. Exposure of the original acid without a solvent yields slowly, without the formation of a colored intermediate, a crystalline dimer isomeric with that formed in benzene solution.

In the presence of oxygen, the benzene solution forms, in addition to the dimer a bromoacid, apparently by the addition of the elements of hypobromous acid to the original unsaturated acid. When the benzene contains moisture, colorless crystals of a saturated, bromine-free acid, $C_{10}H_{10}O_6$, are also formed by photochemical "hydroxylation" at the double bond.

The polymerization products are cyclobutane derivatives. Ellingboe and Fuson[190] found that ultraviolet light has little or no effect on *trans*-1,2-dibenzoylcyclobutane in benzene. According to Vorländer and Daehn[191] 7-phenylheptatrienic acid and its sodium salt in aqueous suspension are strikingly stable, ultraviolet light decomposing only a small portion.

In benzene solution,[192] 3-phenyl-2-methylindone gives rise to two diphenyldimethyltruxones, one being white and melting at 307-308°C. and the other pale canary-yellow, melting at 259-260°C.





These compounds react with concentrated sulfuric acid to form 3-phenyl-2-methylindone. When the latter is exposed in benzene solution to the action of ordinary sunlight, the truxone melting at 307-8°C. is formed, together with what appeared to be a third isomer, yellow crystals of melting point 174-176°C. A third diphenyltruxone, $C_{30}H_{20}O_2$, yellow needles, m.p. 184-5°C., is obtained when the colorless isomers formed by treating ethyl β,β-diphenyl-lactate with concentrated sulfuric acid are exposed in benzene solution to ultraviolet rays. Ethylphenylindone does not give truxones when irradiated. Prolonged action of ultraviolet light on the 307-8°C. isomer of dimethyldiphenyltruxone in benzene converts it into methylphenylindone.

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[187] Reimer, M., *J. Am Chem. Soc.*, **46**, 783 (1924).

[188] Reimer, M., and Kamerling, H. H., *J. Am Chem. Soc*, **55**, 4643 (1933); Reimer, M., Tobin, E., and Schaffner, M., *Ibid.*, **57**, 211 (1935).

[189] Reimer, M., *J. Am. Chem. Soc.*, **58**, 1108 (1936)

[190] Ellingboe, E., and Fuson, R. C., *J. Am. Chem. Soc.*, **56**, 1774 (1934).

[191] Vorländer, D., and Daehn, E., *Ber.*, **62B**, 545 (1929).

[192] DeFazi, R., *Gazz. chim. ital.*, **54**, 85, 1000 (1924); **57**, 551 (1927).

Bodforss[193] found that benzoylphenylethylene oxide, benzoyl-*m*-nitrophenylethylene oxide, and benzoyl-*p*-chlorophenylethylene oxide undergo rearrangement into phenyl α-hydroxystyryl ketones with increasing readiness when their solutions in methyl alcohol are exposed to a mercury lamp. The yields of the isomers are very small, but their presence can be demonstrated by the ferric chloride test for enols and by the precipitation of copper salts, from which they can be isolated.

Some of these transformations are phototropic, that is, the changes produced by light are reversed in darkness. This is notably the case with the fulgides studied particularly by Stobbe.[194] These are aryl derivatives of butadienedicarboxylic acid. Triphenylfulgide forms orange-red crystals which become dark brown in sunlight or in the rays of an arc lamp and which revert to their original color in darkness. The brown and orange forms seemed to be chemically identical. If the phototropic change is frequently repeated, the difference between the shades of the two forms becomes gradually less, a chemical change taking place which leads finally to the conversion of the fulgide into a new substance, the photoanhydride.

Phototropic change in these compounds was observed only in the case of the lemon-yellow to orange-red diaryl and the orange-red to dark red triarylfulgides; the colorless alphyl, greenish-yellow to yellow monoaryl and red, purple-red or brown or tetraarylfulgides are not phototropic. The modifications of a phototropic substance can exist in the pure state only during exposure to the wave-length of light which forms them since they revert in darkness to a mixture or solid solution of more than one form The equilibrium between the two modifications in a mixture depends on the wave-lengths of light (and their relative intensities) to which it is exposed.

The phototropy of other substances than the fulgides has also been studied by Stobbe.[195] Red and blue rays have no action in reversing the color change produced by ultraviolet light on colorless β-tetrachloro-α-ketonaphthalene, only yellowish-green and yellowish rays being effective A complete discussion of the many instances of phototropy would consume much space [196]

STEREOISOMERISM OF OXIMES

Stereoisomeric changes about the carbon-nitrogen double bond in the benzaldoximes also occur. Ciamician and Silber[197] showed the nitrobenz-*syn*-aldoximes to be changed to the *anti* form when their benzene solutions were exposed in glass tubes to sunlight. (It must be noted that these and other workers used the configurations in the sense opposite to that at present accepted. Thus, they stated that the *anti* forms were converted to the *syn* forms.) Ciusa [198] reported simila changes in the case of *p*-chloro- and 3-nitro-*o*-methoxybenz-*syn*-aldoximes. H was unable to observe the conversion in the case of unsubstituted benz-*syn*-aldoxim or of 3,4-methylenedioxy-*syn*-aldoxime, and inferred that the presence of a negative substituent is necessary for the change to occur. By the use of a quart mercury arc, however, Brady and McHugh [199] showed that this is not the cas and that the conversions can be effected. The change occurred in all but two o a series of 24 aldoximes and their derivatives. 3,4-Dimethoxybenz-*syn*-aldoxim underwent no change [200] and 5-bromo-3,4-dimethoxybenz-*syn*-aldoxime suffere demethylation to 5-bromo-3-methoxy-4-hydroxybenz-*syn*-aldoxime. The methy ether of benzaldoxime is decomposed by ultraviolet with the formation of benzonitrile, but the methyl ether of *m*-nitrobenzaldoxime undergoes no change. Th methyl ethers of *m*- and *p*-nitrobenz-*syn*-aldoximes are partially isomerized, confirming earlier results obtained with sunlight,[201] but not so rapidly or completel as in the case of the oximes themselves. In subsequent work, Brady and Klein [20 succeeded in effecting the conversion in the α-*O*-*p*-nitrobenzyl ethers of *o*-, *m*- an *p*-aldoximes, of 3,4-methylenedioxybenzaldoxime, of *o*- and *p*-methoxybenzaldoxime of 3-nitro-4-methoxybenzaldoxime, and of 5-nitro-2-methoxybenzaldoxime, as wel as in α-*O*-methyl-6-nitro-3,4-methylenedioxbenzaldoxime. Although similar treatment of the α-*O*-methyl-3-nitro-4-methoxybenzaldoxime resulted in partial inversion, the product could not be separated into its components. Brady and Peakin [20 found that, apart from slight but profound decomposition, *m*-nitrobenzodimethyl amidoxime is unchanged by exposure, in benzene solution in a silica vessel for 4 hours to the light of a quartz mercury lamp.[204]

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[193] Bodforss, S , *Ber.*, **51,** 214 (1918), *Chem Abs* , **12,** 2554 (1918); *J Chem. Soc* , **114,** I, 232.

[194] Stobbe, H , *Annalen,* **359,** 1 (1908), *J. Chem Soc.,* **94,** II, 339 (1908).

[195] Stobbe, H , *Ber Verhandl. Sachs Akad Wiss. Leipzig* **74,** 161 (1922); *Chem Abs* , **17,** 3020 (1923)

[196] For details, consult the review articles cited in Chapter 16 For benzylidene-, anisylidene- and cuminylidenehydrazones, see Biltz H , and Wienands, A., *Annalen,* **308,** 1 (1899); *J Chem Soc.,* **76,** 910 (1899); tetraphenyldihydrotriazine, v. Walther, R., *J. Chem. Soc* , **84,** i, 582 (1903); ethyl oxalisobutyrate, Wislicenus, W., and Kiesewetter, M , *J Chem Soc* , **74,** i, 240 (1898); α-azoxynaphthalene, Cumming, W M., and Steel, J. K., *J Chem Soc* , **123,** 2464 (1923); tetrabenzoylethylene, von Halban, H., and Geigel, H., *Z. physik Chem* , **96,** 233 (1920), aminoaryldisulfoxides, Child, R., and Smiles, S., *J. Chem. Soc.,* 2696 (**1926**): diphenylacyldiphenylmethane, de Carvalho, A. P., *Compt rend* , **200,** 60 (1935). For further data on the fulgides, see Dietzel, R , and Naton, J , *Ber.,* **58B,** 1314 (1925), Stobbe, H , Ljungren, G., and Freyberg, J., *Ber.,* **59B,** 265 (1926); α-γ-diphenylallyl ether, Shoppee, C. W., *J. Chem Soc* , 2567 (**1928**). For "reversed phototropy," see Heilbron, I M , and Wilson F. J , *J. Chem. Soc.,* **105,** 2892 (1914) and Heilbron, I. M., Hudson, H E , and Huish, D M., *ibid.,* **123,** 2273 (1923).

[197] Ciamician, G., and Silber, P., *Ber* , **36,** 4268 (1903).

The isomeric changes of the semicarbazones, particularly of cinnamaldehyde have been discussed in previous paragraphs and it has been pointed out that som workers believe the changes can be attributed to tautomerism within the urea portion of the molecule without the necessity of considering stereoisomerism about th double bonds in other portions of the molecule. On exposing solutions of th semicarbazones of dypnone and phenyl-β-phenylstyryl ketone, and the mesity oxide-δ-phenylsemicarbazones to a quartz mercury lamp, Wilson and Macaulay [20 observed that stereoisomers are formed. Attempts to prepare stereoisomers of th semicarbazones of benzylacetone, benzylacetophenone, methyl styryl ketone an styrylisobutenyl ketone gave negative results.

Phototropy is observed in many semicarbazones. Gheorghiu and Arwentiew [206] fin the semicarbazone resulting from the condensation of methyl isobutyl ketone with anisaldehyde to become colored in diffused light, a general property of the semicarbazone of the aldehyde condensation products with ketones in the α- but not in the γ-position Although the semicarbazones of ethylenic ketones of the type ArCH=CHCOR, in whic Ar is aryl and R either alkyl or aryl, resulting from the alkaline condensation of methyl ketones with aromatic aldehydes are phototropic, those of the ketones ArCH=CRCOCH.

[198] Ciusa, R., *Atti R. Accad. Lincei*, **15**, ii, 721 (1906).

[199] Brady, O. L., and McHugh, G. P., *J. Chem Soc.*, **125**, 547 (1924)

[200] See Brady, O. L., and Dunn, F. P., *J. Chem Soc.*, **123**, 1790 (1923).

[201] Brady, O. L., and Dunn, F. P., *J. Chem. Soc.*, **103**, 1624 (1913).

[202] Brady, O. L., and Klein, L., *J. Chem. Soc.*, 874 **(1927)**.

[203] Brady, O. L., and Peakin, F. H., *J. Chem. Soc.*, 2269 **(1929)**.

[204] For absorption data on various oximes and semicarbazones, see Ramart-Lucas, Mme., and Grume M., *Bull. soc chim.*, **53**, 753 (1933); Ramart-Lucas, Mme., and Bruzau, Mme., *Bull. soc. chim.*, 1 119 (1934). For thiocyanoacetoneoxime, Ponomarev, F. G., Alpatov, D. M., and Strepetov, N. P Acta Univ. Voronegiensis, **9**, No. 3, 132 (1937); *Chem. Abs.*, **32**, 7021 (1938).

[205] Wilson, F. J., and Macaulay, R. M., *J. Chem. Soc.*, **125**, 841 (1924).

[206] Gheorghiu, C. V., and Arwentiew, B., *Ann. sci. Univ. Jassy*, **16**, 536 (1931); *Chem. Abs.*, **26**, 4804 (1932); see also Dickinson, R., Heilbron, I. M., and Irving, F., *J. Chem. Soc.*, 1888 **(1927)**.

obtained by acid condensation are stable to light.[207] Since the phototropy is connected with the presence of double bonds conjugated with the benzene nucleus, all changes disturbing the conjugation tend to diminish or eliminate the phenomenon. It is probable that the phototropic change consists in a shift of the valence electrons brought about by the action of light.

The thiosemicarbazones and δ-phenylsemicarbazones of the ethylenic ketones of the type ArCH=CHCOR are always phototropic.[208]

AROMATIC AMINES

The spectrum of aniline vapor includes 185 lines and bands between 1980 and 2632A and a continuous zone from 2632A.[209] Savard found for the excitation energies of three electronic states 97.9, 99.2 and 102 kcal. The energy of dissociation into C_6H_5NH and a hydrogen atom is 108 kcal.[210]

By studying the change in the ultraviolet absorption of solutions with change in pH, Hammett, Dingwall and Flexser[211] determined its dissociation constant. The well-known photochemical discoloration of aniline[212] is believed to be an oxidation. It is furthered by the presence of *o*- and *p*-phenylenediamine as impurities, but is retarded by the *m*-isomer and is almost completely inhibited in the absence of oxygen. It is also retarded by minute amounts of sodium sulfide or oxalic acid, or by contact with emery-surfaced zinc or iron plates, either untreated or previously boiled with 20-per cent sodium sulfide. On the other hand, if iron plates are cleaned by heating with dilute sulfuric acid, they accelerate the reaction even though they have been treated with sodium sulfide. Mild heating over a gas flame somewhat restores the preserving action. Partially rusted iron plates after boiling with 20-per cent sodium sulfide also retard the oxidation. These experiments were conducted to develop methods for the storage and transportation of aniline in iron drums. In the method recommended, the drums were flushed with hot water, and without further cleaning were boiled with 5- to 20-per cent sodium sulfide, sealed, allowed to cool, emptied, flushed with water and then twice with aniline and filled as soon as possible to avoid oxidation of the iron sulfide film. Yamanaka[213] believes light of the range 5100 to 3000A, and especially 4957 to 4300A to be most effective in producing the color. On the other hand, Freytag,[214] by exposing strips of hardened filter paper impregnated with aqueous or alcoholic solutions of 18 primary amines behind a quartz spectrograph, found the majority of them to be sensitive only to ultraviolet light of wave-lengths less than 3130A. The intensity of the color developed varied greatly with the wave-length employed. He finds[215] ultraviolet to markedly accelerate aniline black dyeing. Photographic negatives may be printed on cotton fabric impregnated with a 1- to 25-per cent solution of aniline hydrochloride containing five drops of potassium ferricyanide and 18 to 24 drops of 10-per cent aqueous potassium chlorate solution per 30 cc., exposing for fifteen minutes to ultraviolet light and washing away the unchanged aniline with water.

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[207] Gheorghiu, C. V., *Bull. soc chim*, **53**, 1441 (1933).

[208] Gheorghiu, C. V., *Bull. soc. chim.*, **1**, 97 (1934).

[209] Savard, J., *Compt. rend*, **190**, 678 (1930); *Bull. soc. chim.*, **53**, 1404 (1933).

[210] See also, Horio, M., *J Soc. Chem. Ind. Japan*, **37**, Suppl 284 (1934). For a comparison of the spectra of aniline and acetanilide, see Klingstedt, F. W., *Z. physik. Chem.*, **1B**, 74 (1928). Benzylamine, Ley, H., and Volbert, F., *Ber.*, **59B**, 2119 (1926) Nitrosodimethylaniline, Custers, J. F. H., and Dippel, C. J., *Z. Physik*, **86**, 516 (1933). Nitroanilines, Glotz, G., *Bull. soc. chim.*, **1**, 1148 (1934). Toluidines, Morton, R. A., and McGookin, A., *J. Chem Soc.*, 901 (**1934**). Arylamines, Ramart-Lucas, Mme., and Wohl, Mlle., *Compt. rend.*, **196**, 1804 (1933). For fluorescence studies on amines, see Lumière, A., Lumière, L., and Seyewetz, A., *Bull. soc. chim.*, **37**, 700 (1925).

[211] Hammett, L. P., Dingwall, A., and Flexser, L., *J. Am Chem. Soc*, **56**, 2010 (1934).

[212] Bulich, P. K., *Anilinokrasochnaya Prom.* **3**, 405 (1933); *Chem. Abs.*, **28**, 1335 (1934).

[213] Yamanaka, T., *Bull Inst. Phys-Chem. Research (Tokyo)*, **14**, 396 (1935); *Chem. Abs.*, **30**, 1754 (1936).

[214] Freytag, H., *Z. wiss. Phot.*, **33**, 33 (1934); *Brit. Chem. Abs.*, **1934A**, 740.

[215] Freytag, H., *Melliand. Textilber.*, **13**, 144 (1932); *Chem. Abs.*, **27**, 1834 (1933).

The reactions between aniline and nitrobenzene which occur during a five months' exposure to summer sunlight in sealed tubes have been studied by Vecchiotti and Piccinini.[216] The liquid became red-brown but was neutral in reaction and evolved no gas. Among the compounds identified were, besides unchanged nitrobenzene and resin, *o*-hydroxyazobenzene, azoxybenzene and a small quantity of *p*-aminophenol. The results are explained by regarding the initial reaction as a simultaneous oxidation and reduction of nitrobenzene forming nitrosobenzene and phenylhydroxylamine. The nitrosobenzene reacts with the phenylhydroxylamine to yield water and azoxybenzene, the latter then transforming into *o*-hydroxyazobenzene. The great tendency of phenylhydroxylamine to change to *p*-aminophenol accounts for the presence of this material. Decomposition products of nitrosobenzene probably enter into other secondary reactions.

In the reaction between toluene and nitrobenzene there were obtained,[217] in addition to benzoic acid and *p*-aminophenol, aniline and azoxybenzene. The benzoic acid is formed by oxidation of toluene by nitrobenzene which is reduced to nitrosobenzene. A molecule of unaltered nitrobenzene reacts with three of benzaldehyde, an intermediate oxidation product, to produce two of benzoic acid and one of benzoylaniline. The latter is then hydrolyzed to aniline and benzoic acid. Benzoylaniline also may be formed along with benzoic acid by the interaction of nitrosobenzene with two molecules of benzaldehyde.[218] Azoxybenzene may be formed either by the interaction of nitrosobenzene and benzaldehyde or, by analogy with the reaction of nitrosobenzene and phenylhydroxylamine, by the interaction of nitrosobenzene and benzoylphenylhydroxylamine It might also be produced by a reaction between nitrosobenzene and *p*-$OHC_6H_4NHCOC_6H_5$. The compounds required for the last two processes were not isolated although their formation is conceivable. According to Knipscheer,[219] *o*-hydroxyazobenzene is formed by the action of light on azoxybenzene, but it was not identified by the Italian observers The aniline is partly oxidized to phenylhydroxylamine, which under the influence of light, forms *p*-aminophenol.

The action of sunlight for six months on a mixture of *o*-nitrotoluene and aniline gave a product containing *p*-aminophenol, 2′-methylazoxybenzene, and an isomer of the latter, probably a benzeneazocresol.[220]

Plisov [221] made some preliminary experiments on the photochemical formation of salts of aromatic amines with alkyl halides in an attempt to determine whether the activation of the amine or of the halide is the determining factor in the reaction. Photochemical action is more evident in the combination of aniline with benzyl chloride than in the case of *o*-toluidine and benzyl chloride. In the former case, the yield in three hours increased from 15 per cent in darkness to 82 per cent under irradiation in a quartz vessel by an arc.

Migrations in N-Substituted Amines. Blanksma [222] has noted that acetylchloroaminobenzene is altered by light, following the general rule that the radicals

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[216] Vecchiotti, L., and Piccinini, C., *Gazz. chim ital.*, **61**, 626 (1931).

[217] Vecchiotti, L., and Zanetti, G., *Gazz. chim. ital*, **61**, 798 (1931).

[218] Bamberger, E., *Ber.*, **35**, 1606 (1902); Ciamician, G., and Silber, P., *Atti accad. Lincei*, **14**, 265 (1905).

[219] Knipscheer, H. M., *Rec trav. chim*, **22**, 1 (1903)

[220] Vecchiotti, L., and Piccinini, C., *Gazz. chim. ital.*, **63**, 112, 319 (1933); *Brit. Chem Abs.*, *A*, 602 (1934).

[221] Plisov, A. K., *Gazz. chim. ital.*, **59**, 200 (1929); *Chem Abs.*, **23**, 4198 (1929).

[222] Blanksma, J. J., *Proc. K. Akad. Wetensch. Amsterdam*, **5**, 178 (1902); *J. Chem. Soc.*, **82**, II, 646 (1902).

Br, Cl, NO_2, NO and O, attached to nitrogen, change places, under the influence of sunlight, with a hydrogen atom in the nucleus. Chattaway and Orton also made some velocity measurements on the transformation of the compound in sunlight,[223] and had previously studied the thermal reaction for which Armstrong[224] found a trace of hydrogen chloride essential. Mathews and Williamson[225] have studied the reaction in solutions in benzene, alcohol and acetic acid, using a quartz mercury lamp. The solvent exerts a marked effect, but hydrochloric acid is not required for the photoreaction. The addition of water to an alcoholic or glacial acetic acid solution greatly diminishes the velocity of the photo-decomposition. In the absence of water, the reaction in these solvents proceeds without the action of radiation, after having been started in this manner. In the presence of water, this effect is lacking and the reaction is truly photochemical.

Porter and Wilbur,[226] who presented data on the absorption of ultraviolet by acetylchloroaminobenzene and its rearrangement product, found the transformation to occur in the solid phase as well as in solution. Hodges[227] found the rate of the change under the influence of the 3569A line in eight solvents very slow in the complete absence of water. It is a chain reaction, the quantum yields being 5-6 in carbon tetrachloride, 15-18 in bromobenzene, 17 in chloroform, 22 in chlorobenzene, 29-33 in benzene, 108-116 in toluene, 156-163 in cyclohexane, and 188 in decalin. In closely related solvents, the reaction velocity diminished with increasing dielectric constant, surface tension and density.

Condensation Reactions of Amines. The condensation of *p*-phenetidine hydrochloride with epichlorohydrin to N,N-*bis*(γ-chloro-β-hydroxypropyl)-*p*-phenetidine is accelerated by sunlight.[228]

Qualitative observations on the nature of the products formed by the prolonged exposure to tropical sunlight of a number of organic compounds in 2 per cent solutions in water, dilute acid or alkali or alcohol have been recently reported by Malaviya and Dutt.[229] Aniline in hydrochloric acid precipitated phenazine in 135 days, *o*-toluidine gave 1,5-dimethylphenazine, *m*-toluidine, 2,6-dimethylphenazine and *p*-toluidine probably gave 3,7-dimethylphenazine. Dimethylaniline did not change in 141 days and 1,3,4-xylidine gave only a trace of precipitate in 121 days. α-Naphthylamine probably gave α,β-dinaphthazine and β-naphthylamine probably β,β-dinaphthazine. *o*-Nitraniline was unaffected *p*-Nitrosodimethylaniline in aqueous solution was oxidized to *p*-nitrodimethylaniline, but in dilute acid, it gave an unidentified precipitate and benzidine gave an unidentified phenazine. In dilute acid, *o*-phenylenediamine gave 2,3-diaminophenazine hydrochloride, the *m*-compound 2,6-diaminophenazine and the *p*-compound probably 3,6-diaminophenazine. *p*-Aminodimethylaniline gave an intensely violet solution of an unidentified azine dye. Aqueous *p*-amino-acetanilide gave diacetyl-*p*,*p*'-diaminodiphenylamine. 1,8-Diaminonaphthalene gave a brown precipitate, probably *peri*-dinaphthalene azotide. *o*-Aminophenol formed a red compound, $C_{24}H_{18}N_3O_2$, the *m*-compound an unidentified brown precipitate, and the *p*-compound a violet precipitate, probably *p*,*p*'-dihydroxydianilinoindophenol. *m*- and *p*-Hydroxydimethylanilines were unaffected. 1,5-Dimethoxyphenazine was formed from *o*-methoxyaniline, the 3,7-compound from the *p*-derivative and corresponding diethoxyphenazines were produced from the ethoxy-compounds. 2,4-Hydroxyphenylenediamine gave an unidentified phenazine. Aminobenzoic acid gave phenazine-1,5-dicarboxylic acid, the *m*-compound did not alter, but the *p*-acid in alkaline solution gave the sodium salt of *p,p'*-azobenzenedicarboxylic acid.

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[223] Chattaway, F D., and Orton, K. J. P., *Proc Chem. Soc*, **81**, 200 (1902).

[224] Armstrong, H E., *J. Chem. Soc.*, **77**, 1047 (1900).

[225] Mathews, J H., and Williamson, R, *J Am Chem Soc.*, **45**, 2574 (1923)

[226] Porter, C. W, and Wilbur, P, *J. Am Chem Soc.*, **49**, 2145 (1927)

[227] Hodges, F. W., *J. Chem. Soc*, 240 (1933).

[228] Strukov, I. T., *Khim. Farm. Prom.*, No. 2, 11 (1934); *Chem. Abs.*, **28**, 5421 (1934).

[229] Malaviya, B. K., and Dutt, S., *Proc. Acad. Sci. United Provinces Agra Oudh, India*, **4**, 319 (1935); *Chem. Abs.*, **30**, 1056 (1936).

Vanillin, 2,4-dihydroxybenzaldehyde and *p*-dimethylaminobenzaldehyde were unchanged. Aqueous *p*-aminobenzaldehyde hydrochloride gave *p,p'*-dialdehyde-azobenzene.

Aqueous 1-per cent eosin was decolorized in 75 days, giving hydrogen bromide and a precipitate of 2,4-dibromobenzoylbenzoic acid. Similarly erythrosine gave hydrogen iodide and probably 2,4-diiodobenzoylbenzoic acid. *p*-Aminoacetophenone gave an unidentified precipitate, capable of reducing ammoniacal silver nitrate, but gallacetophenone was unaffected. Phenylhydrazine evolved nitrogen and formed an unidentified, apparently heterocyclic nitrogen compound. 2-Aminothiazole gave a trace of a phenazine derivative. Aqueous thiocarbamide gave sulfur and carbamide in 46 days. α-Benzildioxime in dilute alkali gave 3,4-diphenylfurazan in 35 days.

Color Reactions of Amines. Schall[230] proposed to test for ultraviolet rays by their ability to form a blue coloration on filter paper impregnated with *p*-phenylenediamine nitrate (2/3*N*) and dried. Such paper is sensitive only to wave-lengths shorter than 3130A. Diffused daylight produces only a pale gray tint but a quartz mercury lamp produces a blue color in an instant. Mott and Bedford[231] made the paper by impregnating white blotting paper in a solution of 1 g. *p*-phenylenediamine, 3 cc. of water and 2 cc. of nitric acid, s.g. 1.21, and drying one-half hour in a steam oven.

Freytag[232] states also that irradiation of moist filter paper or cotton fabric impregnated with solution containing about 0.1 per cent of either phenylenediamine, or their mixtures, resulted in yellow to brown color formation due to oxidation of the base. This was assisted by the presence of 0.1 per cent sodium nitrate and potassium nitrate. The resulting colors were faster to washing when aniline was also present. The process could be adapted to the production of photographic prints on fabric.

Nile-blue, brilliant green, Capri-blue, phenosofranine, fuchsin and pinakryptol-green are negative catalysts toward the photochemical decomposition of "Aktivin," sodium *p*-toluenesulfonchloroamide, in methanol solution.[233] Malachite-green had no effect, and pinakryptol-yellow and methylene-blue were positive catalysts, even in darkness.

The photochemical oxidation of aqueous solutions of benzidine in the presence of eosin is accelerated by manganese salts and by iron and copper salts in decreasing quantities.[234] Eosin, chlorophyll and the fluorescent derivatives of the latter bring about the oxidation of benzidine in methanol. Green leaves in water solutions of benzidine also bring about its oxidation when illuminated.

Picric acid, in solutions at pH 13.0, is decomposed in ultraviolet light to give picramic and isopurpuric acids, nitrous acid, ammonia and hydrogen cyanide. The usual yellow form present at lesser pH values is unaffected.[235] An analogous reaction occurs with 2,5-dinitrophenol. *o*- and *p*-Nitrophenols, 2,4- and 2,6-dinitrophenols and 2,4-dinitro-*o*-cresols decompose at reactions at which the red forms exist, the rate increasing with the pH. These darken with the formation of an amino- group.

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[230] Schall, C., *Photograph. Wochenblatt*, **33**, 321 (1907), *Chem. Ztg.*, **34**, 267; *Z. physik. Chem. Unterr*, **21**, 389 (1908).

[231] Mott, W. R., and Bedford, C. W., *J. Ind. Eng Chem.*, **8**, 1029 (1916).

[232] Freytag, H., *Melliand. Textilber.*, **13**, 322 (1932), *Chem. Abs*, **27**, 1834 (1933).

[233] Milbauer, J., *Phot. Korr.*, **71**, 94 (1935); *Brit. Chem. Abs.* **A**, 1468 (1935); *Chem. Listy*, **29**, 267 (1935); *Chem. Abs.*, **30**, 1661 (1930)

[234] Noack, K., *Phot. Korr.*, **62**, 73 (1926); *Chem. Abs.*, **21**, 1409 (1927).

Textiles of animal or vegetable fibers impregnated with nitrophenols, nitroamines, or even colorless nitro- compounds, turn brown when exposed to daylight or ultraviolet rays.[236] Reduction apparently takes place, as reducing agents hasten, and oxidizing agents retard, the effect. The brown substance thus formed from picric acid on calico was isolated, by extraction with alkali and precipitation with acid, and found to contain nitro- or nitroso- groups, but no amino- group. This substance may be an azo- compound derived from an azoxy-reduction product of picric acid.

Azo, Diazo and Related Compounds. Knipscheer[237] has shown that azoxybenzene is converted by light into *o*-hydroxyazobenzene. He obtained the latter in poor yield (10.3 per cent) and with much loss of material by volatilization (39.7 per cent) by exposing sheets of filter paper impregnated with azoxybenzene to sunlight for five weeks. Cumming and Ferrier,[238] who believed the loss by volatilization could be obviated by making the exposures in solution, employed a mercury vapor lamp as source. The best results (28.0 per cent) were obtained by 50 hours' exposure in absolute ethanol and the smallest (7.7 per cent) with benzene as solvent. Increase of temperature improved the yield only slightly, but materially increased the loss of azoxybenzene by volatilization. The transformation also takes place in sunlight, but cannot be effected by an ordinary electric light.

The action of light on the α-isomer of benzeneazoxy-*p*-toluene, $NC_6H_4O{=}N.C_6H_4CH_3$ yields a red substance, probably an *o*-hydroxy- compound.[239] The β-isomer, $NC_6H_4{=}NO.C_6H_4CH_3$, very slowly turns yellow.

Cumming and Ferrier also obtained hydroxyazo- compounds from 2,2′-, 3,3′- and 4,4′-azoxytoluenes, 4,4′-dichloroazoxybenzene and 2,2′-diamino-4,4′-azoxytoluene. 4,4′-Azoxyanisole, 4,4′-azoxyphenetole, and 4,4′-dinitroazoxybenzene reacted slightly or not at all. In the case of 2,2′-azoxytoluene, products of widely different melting points were obtained in alcohol and in benzene as solvents. The hydroxyazo- compounds were obtained as red needles of varying solubility in sodium hydroxide solution. In cases in which the orientation could be determined, the hydroxyl group appeared to enter the benzene nucleus in the ortho position with respect to the azo-group.[240]

The decomposition of a 0.4 per cent solution of diazosulfanilic acid in ultraviolet light is proportional to the time of irradiation until 90 per cent has been decomposed; the remainder condenses with the phenol produced.[241] At pH values less than 7, the diazo- solution is very sensitive to light, but relatively stable to heat, while in alkaline solutions, the reverse is true. Similar results are obtained at 35°, 56°, 80° and 100°C., but when the temperature approaches that at which thermal decomposition of the diazo- compound occurs, this action predominates. Substitution of negative radicals in the benzene nucleus, which increases the stability of the diazo- compound to heat, decreases its stability to light, the order of increasing stability being *p*-OH (anhydride) $<$ *p*-SO_3H (anhydride) $<$ *p*-COOH (anhydride) $<$ *p*-Cl (chloride) $<$ *p*-NO_2 (chloride) $<$ benzenediazonium chloride. Decomposition is complete only in the first two cases. The effect of the nitro- group is the same in the ortho, meta and para positions. Decomposition by light of the diazo- compounds derived from sulfanilic acid, *p*-aminophenol, and aniline yields the corresponding phenol as in thermal decomposition; the derivative of *p*-aminobenzoic acid yields *p*-hydroxy- and *p*-chlorobenzoic acids, while from the brown precipitate obtained by decomposition of nitrobenzenediazonium chlorides is isolated a substance which is probably dinitrodiphenyl ether.

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[235] Molnar, J., *Compt. rend.*, **201**, 1482 (1935).

[236] Seyewetz, A., and Mounier, D., *Compt. rend.*, **185**, 1279 (1927).

[237] Knipscheer, H. M., *Rec. trav. chim.*, **22**, 1 (1903).

[238] Cumming, W. M., and Ferrier, G. S., *J. Chem Soc.*, **127**, 2374 (1925).

[239] Bigiavi, D., and Sabatelli, V., *Gazz chim. ital.*, **57**, 557 (1927); *Chem. Abs.*, **22**, 395 (1928).

[240] See also Ramsperger, H. C, for some determination of reaction rates for the thermal and photochemical decomposition of azo- compounds, *Proc. Nat. Acad. Sci.*, **13**, 849 (1927).

[241] Seyewetz, A., and Mounier, D., *Compt. rend.*, **186**, 953 (1928); *Bull. soc. chim.*, **43**, 827 (1928); *Brit. Chem. Abs.*, **1928A**, 493.

By comparing the absorption spectra before and after photolysis, Fukushima and Horio[242] concluded that the photodecomposition of diazobenzene sulfonic acid differs from the thermal reaction. It is effected by radiations of wave-length shorter than 3800A. The reaction is of zero order. An inner filter, such as quinine sulfate, retards the photolysis. The effects of temperature are complex.

Azo compounds may be photosensitized by zinc oxide, according to Fukushima, Horio and Omori.[243] In dilute alcoholic solution and an oxygen-free atmosphere in the presence of zinc oxide, azobenzene was reduced almost quantitatively to hydrazobenzene, but with pure oxygen there was no reduction in six months.[244]

Lyashenko and Kirzner[245] carried out the photolysis of phenyldiazonium chloride and its *o*-, *m*-, and *p*-substituted derivatives under exactly similar conditions by exposing the diazo- solutions for three hours to the action of daylight and the light of a mercury vapor lamp. The nitrogen eliminated was measured. They found that substitution in the meta position either increases the stability of aniline to light or has no influence. Substitution in the ortho and para positions decreases it. The ethoxy- group in the para position has no effect.

Other Compounds. The condensation products of aromatic thiohydrazide with aldehydes, ketones, and sugars on irradiation with the lines 6250, 5950 and 5430A exhibit a rapid drop of the rotatory power from a high value in one direction through zero to a maximum in the opposite direction.[246] Continued exposure causes the rotation again to reach zero and then to attain a maximum in the initial direction, after which it slowly drops off to zero. This is explained as a combination of partial racemization, *cis-trans* isomerization and a change in structure, all of which are affected by light.

2,2′-dinitro-5,5′-dimethoxydiphenyl disulfide rapidly turns yellow in sunlight.[247]

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[242] Fukushima, I., and Horio, M., *J. Soc. Chem. Ind. Japan*, **34**, *Suppl. binding*, 367, 372, 374 (1931), *Chem. Abs.*, **26**, 2377 (1932).

[243] Fukushima, I., Horio, M., and Omori, M., *J. Soc. Chem. Ind Japan*, **35**, *Suppl. binding*, 398 (1932); *Chem. Abs.*, **26**, 5848 (1932).

[244] The formation of equilibrium between *cis* and *trans* forms of azobenzene can be activated by light Hartley, G. S., *Nature*, **140**, 281 (1937); von Auwers, K., *Ber.*, **71B**, 611 (1938); Cook, A. H., *J Chem. Soc.*, 876 (**1938**).

[245] Lyashenko, V. D., and Kirzner, N. A., *Anilinokrasochnaya Prom.*, **4**, 272 (1934); *Chem Abs.*, **28**, 7164 (1934).

[246] Lifschitz, I., and Froentjes, W., *Rec trav chim*, **55**, 753 (1936)

[247] Hodgson, H. H., and Handley, F W, *J Chem. Soc.*, 542 (**1926**).

Chapter 26

Compounds with Condensed Ring Systems

NAPHTHALENE DERIVATIVES

There appear to be no descriptions of photochemical reactions of naphthalene. However, its absorption spectrum and also spectra of many of its alpha- and beta-derivatives have been investigated by de Laszlo.[1] Its vapor exhibits about 400 sharp narrow bands with fine structure between 3200 and 2820A and a group of broad continuous bands without fine structure between 2820 and 2500A.

Although naphthalene vapors are stable to the light of the quartz mercury arc, 1,2- and 1,4-dihydronaphthalenes quickly decompose to naphthalene. Tetralin decomposes more slowly, forming unidentified polymerization products.[2]

A number of nitro- derivatives of naphthalene are light-sensitive, producing brown colors which result from the reduction of nitro- groups. Much work has been devoted to the study of the mutual effects of nitro- and sulfonic acid groups in various positions upon the light sensitivity. One of the earliest instances observed was that in which yellow dyeings on wool of 1,6,4,8-diaminonaphthalenedisulfonic acid became brown rapidly on insolation.[3] The mono-nitro-derivatives of α- and β-naphthalenesulfonic acid are equally sensitive, but 2,4,8-dinitronaphthalenesulfonic acid is fast to light. Since, however, 1,8-nitronaphthalenesulfonic acid is highly sensitive, although the 1,5- compound is not, and since the 1,6- and 1,7- compounds are nearly equally sensitive, the degree of sensitiveness appears to be related to the positions of the nitro- and sulfonic acid groups in the nucleus.

The nitrosulfonic acids are said also to be sensitized to light by the addition of aromatic amines, due to oxidation of the amines by the nitro- group. The corresponding sulfinic acids and sulfonamides also give light-sensitive dyeings.

In the benzene series,[4] the sensitiveness to light decreases in the order ortho, para and meta, while the sensitiveness of *o*-nitrobenzenesulfonic acid is equal to that of *o*-nitrobenzenedisulfide, although considerably less than that of 1,8-nitronaphthalenesulfonic acid. It was suggested that the sensitiveness to light is imparted by the sulfur molecule rather than by the sulfonic group as a whole. The sensitiveness of 1,2-nitronaphthalenesulphonic acid and its salts is but little less than that of the 1,8-compound. Substitution of the hydrogen atom in the sulfonic acid group does not affect the photochemical properties of the nitrosulfonic acids, but the close proximity of the nitro- and sulfonic acid groups in the same ring has a positive influence on it. The dark precipitate formed by irradiation of the 1,8-compound is probably 1 amino-8-(8-nitro-1-naphthylsulfonyl)-2-naphthol, or an isomer containing another hydroxyl group and an NO instead of an NO_2 group. When the magnesium salt of 1,8-nitronaphthalenesulfonic acid is exposed to sunlight, the dark precipitate is probably the cyclic magnesium salt of 2-hydroxy-1,1′-azonaphthalene-8,8′-disulfonic acid.

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[1] de Laszlo, H. G., *Compt. rend.*, **180**, 203 (1925); *Z. physik. Chem.*, **118**, 369 (1925); *Proc. Roy. Soc.*, **111A**, 355 (1926). See also Charlampowiczowna, B., and Marchlewski, L., *Bull intern. acad. Polonaise.* **A**, 376 (1930); Obreimov, I., and Prichotjko, A., *Physik. Z. Sowj.*, **1**, 203 (1932), Kimura, S., *Mem Coll. Sci. Kyoto Imp. Univ.*, **14**, 303 (1931); *Chem. Abs.*, **26**, 1516 (1932).

[2] Kemula, W., and Dunicz, B. L., *Z. physik. Chem.*, **A181**, 359 (1938)

[3] Vorozhtzov, N. N., and Gribov, K. A., *J. Gen. Chem. (U.S.S.R.)*, **2**, 929 (1932), *Chem. Abs.*, **27**, 2440 (1933).

[4] Vorozhtzov, N. N., and Kozlov, V. V., *J. Gen. Chem. (U.S.S.R.)*, **2**, 939 (1932), **7**, 996, 1610 (1937); *Chem. Abs.*, **27**, 2440 (1933), **31**, 5349, 8528 (1937); *Org. Chem. Ind. (U.S.S.R.)*, **4**, 399 (1937).

The change occurs better on wool than on silk or cotton, but it can also be observed in aqueous solutions of the salts, especially the magnesium salt. The reaction is faster in neutral or alkaline than in acid solutions. It is hindered by oxidants. When the substituents are in the "quinogenic" (1,5 and 1,7) positions, the acid is less sensitive than when they are in the 1,6 and 1,8 positions. When paper soaked in these solutions and exposed to light is rinsed with dilute sodium bichromate solutions, the colors are set better than if pure water is used. Nitroanthracene-1-sulfonic acid forms a dark compound when exposed to light, but *meso*-nitro-anthracene-2-sulfonic acid gives a colorless compound.

Steiger[5] studied a number of these compounds, as well as some containing the nitro- group and, in place of or in addition to the sulfonic acid group, the methyl group. The 1,8-nitromethylnaphthalene is more sensitive than *o*-nitrotoluene and nitronaphthalene. Its 5-sulfonic acid also is extremely sensitive. Pyridinium 1-nitronaphthalene-8-sulfonate and the corresponding N-methylpyridinium salt, like potassium 1-nitronaphthalene-8-sulfonate, are also very sensitive. Compounds of the series 5,1,8-$C_{10}H_5(NO_2)SO_2X$ with a substituent in position 5 are more sensitive than those without it. The sensitivity varies with the group X and with the solvent employed.

Data for the absorption of twenty substituted 1,2- and 1,4-naphthaquinones have been given by Beck, MacBeth and Winzor.[6] These observations played a part in the determination of the structures of two dyes, droserone and hydroxydroserone, derived from the insectivorous plant, *Drosera whittakeri*.

The substituted naphthoquinone, 2-methyl-1,4-naphthaquinone, gradually loses its color in sunlight.[7] After two months, ether removed a colorless irradiation product, melting at 235°C. It is a dimer formed by 3,4-addition of two molecules of the naphthaquinone and contains a cyclobutane ring. That the quinone carbonyl groups did not function in the dimerization was shown by the formation of a tetraoxime of the dimer. These observations were made in the course of an investigation of the structure of the pigment phthiocol of the tubercle bacillus.

Dilute aqueous solutions of 2-hydroxy-1,4-naphthaquinone at 70°C. on exposure to ultraviolet light give isonaphthazarin and mainly, 3,3′-dihydroxy-2,2′-dinaphthyl-1,4,1′,4′-diquinone.[8]

When the reaction product of 3-chloro- or 3-bromo 1,2-naphthoquinone and 2,3-dimethylbutadiene in chloroform is heated at 100°C. in sunlight, the red solution becomes yellow in about 45 minutes, then changes to red and finally becomes yellow again. After five hours there results 36 per cent of 2,3-dimethyl 1,4,11,12-tetrahydrophenanthrenequinone-11,12-*endo*-2′,3′-dimethyl-2′-butene. In the dark, 16 to 20 hours of heating would be required. The product is a brilliant yellow, changing to nearly colorless on exposure to the light.[9]

An acid formed by the action of alkali and red mercuric oxide on 4-methyl-β-naphthopyrone followed by treatment with hydrochloric acid, when dissolved in chloroform, is converted into 4-methyl-β-naphthopyrone to the extent of 70 per cent by the action of ultraviolet rays. On the other hand, a modification of the original acid, which melts at 146°C. rather than 112°C. and which is regarded as having the *cis* configuration, is unaltered when similarly treated.[10] It is suggested that the *trans* form is converted into the *cis* form during irradiation. The molecules of the latter may, however, be activated in such manner that the transformation does not stop at this stage, but proceeds further until cyclization to the stable coumarin-type of molecule has been effected. On the other hand, irradiation does not appear capable of activating the molecules of the *cis* form to the extent necessary for formation of the pyrone.

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[5] Steiger, R. E., *Helv Chim. Acta,* **16,** 793, 1315 (1933); **17,** 701, 1354 (1934).

[6] Beck, A. B , MacBeth, A. K., and Winzor, F. L., *Australian J. Exptl. Biol. Med. Sci.,* **12,** 203 (1934); *J. Chem Soc.,* 325, 334 (**1935**).

[7] Madinaveitia, J , *Rev. acad. cienc. Madrid,* **31,** 617 (1934); *Chem. Abs ,* **29,** 5138 (1935); *Anales soc. espan. fis. quim.,* **31,** 750 (1933); *Chem. Abs.,* **28,** 1036 (1934).

[8] Hooker, S. C., *J. Am. Chem. Soc.,* **58,** 1212 (1936).

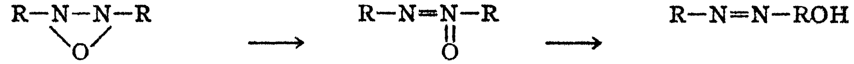
[9] Fieser, L. F., and Dunn, J. T., *J. Am. Chem. Soc ,* **59,** 1021 (1937).

Aqueous solutions of sodium naphthionate undergo a change in surface tension in light. By placing a drop of the liquid in a horizontal capillary tube and exposing one meniscus to light from a mercury arc, Grumbach and Schlivitch[11] estimated the increase in surface tension by the speed of motion toward the lighted end. It is of the order of 1 to 2 mm. per hour. Aqueous solutions of fluorescein, sulfofluorene and uranyl nitrate, xylene solutions of anthracene and alcoholic solutions of xylene and gasoline behave in a similar manner but solutions of ferric chloride or oxalic acid do not.

The ammonium salt of α-nitrosonaphthylhydroxylamine reddens when applied to filter paper and exposed to the rays from a quartz mercury-vapor lamp. Rays of wave-lengths transmitted through glass are effective in producing this change.[12]

β,β-Azoxynaphthalene, which has a pure yellow color and melts at 164°C. on exposure to light (preferably in alcoholic solution) is converted irreversibly into a red isomer melting at 162°C. Both forms are stable toward alcohol in the dark.[13] The α,α′-azoxynaphthalene undergoes a change to a red form[14] regarded as a hydroxyazonaphthalene. Despite the fact that attempts to characterize the red modification as such by benzoylation or methylation failed, support for this structure is afforded by a comparison of the absorption spectra of both forms with that of β-naphthaleneazo-β-naphthol.

Cumming and Steel,[15] however, note that exposure of the α,α′-azoxynaphthalene to sunlight or to the light of a mercury-vapor lamp for a short period produced a red isomer of the same melting point. Further exposure produced an azonaphthol, melting at 224°. This change they formulate:



Yellow azoxynaphthalene *Red isomer* *Azonaphthol*

1,2,7,8-Di-(1′,5′-tetrazolo)-4-methyl-(1,8-naphthyridine, 1,2,7,8-tetrahydride), a light yellow material, becomes brown in a few days in air and light.[16]

Exposure to light converts β-2-hydroxy-1-naphthylcrotonic acid completely into 4-methyl-β-naphthopyrone, if sufficiently prolonged. β-Dimethylcoumaric acid yields 4,7-dimethylcoumarin.[17]

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[10] Dey, B. B., and Lakshminarayanan, A. K., *J. Indian Chem Soc.*, **11**, 373 (1934); *Chem. Abs.*, **28**, 6145 (1934).

[11] Grumbach, A., and Schlivitch, S., *Compt. rend.*, **181**, 241 (1925).

[12] Baudisch, O., and Fürst, R., *Ber.*, **45**, 3426 (1912).

[13] Cumming, W. M., and Ferrier, G. S., *J. Chem. Soc.*, **125**, 1108 (1924).

[14] Baudisch, O., and Fürst, R, *Ber.*, **45**, 3426 (1912).

[15] Cumming, W. M., and Steel, J. K., *J. Chem. Soc.*, **123**, 2465 (1923).

[16] Seide, O., *Ber.*, **59B**, 2465 (1926).

[17] Murty, K. S., Rao, P. S., and Seshadri, T. R., *Proc. Indian Acad. Sci.*, **6A**, 316 (1937); *Chem. Abs.*, **32**, 3362 (1938).

ANTHRACENE

This hydrocarbon differs from naphthalene in exhibiting an interesting polymerization reaction. Anthracene exhibits strong absorption bands at 3800, 3600, 3400 and 3260A.[18] Bands were also found at 4450 and 4750A by Taylor and Lewis,[19] who believed absorption in these bands to be responsible for the occurence of the polymerization reaction. Subsequently, however, it was shown that the latter two bands are due to the presence of chrysogen as an impurity.[20] Capper and Marsh observed that pure white anthracene fluoresces with a violet-blue color, and that the addition of a trace of chrysogen changes this to the familiar magnificent green glow observed in most samples. For this reason, to excite the true fluorescence of anthracene the exciting light would have to be shorter than 4100A. They believed the light effective in polymerization must lie between the first absorption band at 3750A and 3100A since the reaction can be carried out in glass. Castille[21] finds anthracene to exhibit ten bands between 3800 and 2850A and two more in the extreme ultraviolet.[22]

The formation of an insoluble white precipitate when anthracene is irradiated in benzene solution and the recognition that it is dianthracene were subjects of early observations by Fritsche,[23] Elbs,[24] and Orndorff and Cameron.[25] In darkness the polymer yields anthracene by a thermal reaction which goes practically to completion. The process has been employed as a means for the purification of anthracene.[26] A solution of crude anthracene in benzene, toluene or coal-tar naphtha is irradiated by ultraviolet rays, the dianthracene separating and leaving carbazole, phenanthrene and most of the other compounds originally present as impurities in solution. The dianthracene is filtered off and reconverted into anthracene by sublimation, yielding a product of purity of 95 per cent or higher. The method has also been employed for the removal of anthracene from such materials as phenanthrene and fluorene in which it is a contaminant.[27]

The photostationary states set up between the polymerizing photochemical and the depolymerizing thermal reactions in phenetole, anisole and xylene solutions were studied by Luther and Weigert.[28] This is an instance of a photostationary state between two reactions one of which is purely photochemical and the other purely thermal. The depolymerization follows a unimolecular course, is unaffected by light, and has a temperature coefficient of 2.8. The temperature coefficient of the polymerization is only slightly greater than unity. Recently, Lauer and Oda[29] found the polymerization rate to be the same in hexane, cyclohexane, cyclohexene and ethanol. It is considerably greater in acetic acid and, particularly, in benzene. This is attributed to an effect of these solvents in displacing the absorption spectrum of anthracene toward longer wave-lengths. Double bonds in the solvent molecules have a distinct accelerating effect on the reaction. The results in cyclohexene were somewhat uncertain because of a darkening of the solvent. It was also found by Luther and Weigert that in solutions in which absorption was complete a further increase of anthracene concentration tended to increase the rate of polymerization, the rates approaching a limit at higher concentrations. Various early fruitless attempts were made to account for this.[30]

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[18] Hyatt, J. M., *Phys. Rev.*, **19**, 391 (1922).

[19] Taylor, H. A., and Lewis, W. C. M., *J. Am. Chem. Soc.*, **46**, 1606 (1924).

[20] Capper, N. S., and Marsh, J. K., *J. Am. Chem. Soc.*, **47**, 2847 (1925).

[21] Castille, A., *Bull acad roy. med. Belg.*, **8**, 74 (1928); see also Shishlovskil, A. A., *Compt rend acad. sci. U.R.S.S.*, **15**, 29 (1937); *Chem. Abs.*, **31**, 6110 (1937).

[22] For further data on various derivatives, see Barnett, E., Cook, J. W., and Ellison, T. E., *J. Chem Soc.*, 885 (**1928**); Pestemer, M., and Cecelsky, J., *Monatsh.*, **59**, 113 (1932); Clar, E., *Ber.*, **65B**, 503 (1932), **66B**, 202 (1933); Lauer, K., and Oda, R., *Ber.*, **69B**, 137 (1936); Haack, E., *Ber.*, **62B**, 1771 (1929); Barnett, E., Cook, J. W., and Matthews, M. A., *Ber.*, **60**, 2353 (1927); Clar, E., *Ber.*, **62B**, 350 (1929); **63B**, 112 (1930); Clar, E., and Guzzi, A., *Ber.*, **65B**, 1521 (1932); Fieser, L. F., and Hershbarg, E. B., *J. Am. Chem. Soc.*, **57**, 1681 (1935); Obreimov, I., and Prichotjko, A., *Physik. Z. Sowj.*, **1**, 203 (1932).

[23] Fritsche, *J. prakt Chem.*, **101**, 337 (1866)

[24] Elbs, K., *J. prakt. Chem.*, **44**, 467 (1891).

[25] Orndorff, W. R., and Cameron, F. K., *Am. Chem. J.*, **17**, 658 (1893).

[26] Downs, C. R., U. S. P. 1,303,639, May 13, 1919; *Chem. Abs.*, **13**, 1862 (1919).

[27] Capper, N. S., and Marsh, J. K., *J. Chem. Soc.*, 724 (**1926**).

[28] Luther, R., and Weigert, F., *Sitzb. Akad. Wiss. Berlin*, 828 (**1904**); *J. Chem. Soc.*, **86**, ii 463 (**1904**); *Z. physik. Chem.*, **51**, 297 (1905); **53**, 385 (1905).

[29] Lauer, K., and Oda, R., *Ber.*, **69B**, 137 (1936).

Recently, Weigert[31] verified the dependence of the rate upon concentrations in excess of those at which absorption is complete. He employed the lines 3660 and 3130A of the mercury arc. At very low concentrations, below 0.005 per cent, the yield was approximately proportional to the concentration. At higher ones, the rate increased with concentration approaching asymptotically a maximum at about 2 per cent concentration. Between 87° and 137°C., no influence of temperature or solvent was observed. The quantum yields were 0.254 at 3660A and 0.228 at 3130A.

Weigert proposed a more elaborate mechanism for the polymerization than that of Bodenstein who merely assumed that an activated anthracene molecule on collision with a normal one formed the polymer. Weigert assumed that an activated molecule on collision may utilize its activation energy in opening the bond between the two central carbon atoms forming a diradical with two tervalent carbon atoms. Two of these can then unite to produce the polymer.

There is the possibility that this mechanism is unnecessarily elaborate and that the diradical may be directly produced as a result of absorption. Clar[32] suggested that the origin of certain absorption bands is referable to the production of unpaired electrons at the meso- positions. Schönberg[33] assumes a photoequilibrium between the normal and the diradical forms of certain anthracenes, which cannot be magnetically detected because of the small concentration of the diradical form.

When anthracene is irradiated with short wave-lengths (1800 to 2000A), it exhibits a photoelectric effect.[34] At the same time there occurs a surface formation of dianthracene on the crystals. This Suzuki and Volmer[35] regard as an effect secondary to the internal photoelectric effect. They find it possible to prevent its formation by placing metal foils on both sides of the irradiated face and applying a field of 2000-14000 volts per cm.

Behavior of Various Anthracene Derivatives. Polymerization of β-methyl anthracene is a photochemical reaction similar to that of anthracene.[36] 2-3-Benzanthracene in xylene is readily oxidized by air to the quinone with the aid of ultraviolet light.[37] The oxidation of dihydrobenzanthrone is markedly accelerated by light.

[30] Weigert, F., *Z. physik. Chem.*, **63**, 458 (1908); Byk, A., *Ibid.*, **62**, 454 (1908).

[31] Weigert, F., *Naturwiss.*, **15**, 124 (1927).

[32] Clar, E., *Ber.*, **65B**, 503 (1932).

[33] Schönberg, A., *Trans. Faraday Soc.*, **32**, 514 (1936).

[34] Volmer, M., and Riggert, K., *Z. physik. Chem.*, **100**, 502 (1922).

[35] Suzuki, M., and Volmer, M., *Naturwiss.*, **23**, 197 (1935).

[36] Orndorff, W. R., and Megraw, H. A., *Am. Chem. J.*, **22**, 152 (1899); Weigert, F., and Krüger, O., *Z. physik. Chem.*, **85**, 579 (1913).

[37] Clar, E., *Ber.*, **65B**, 503 (1932); **68B**, 2066 (1935).

ANTHRAQUINONES [38]

Anthraquinone has five bands between 4250 and 3600A, one broad band between 3500 and 2850A and four bands between 2800 and 2300A. Methylanthraquinones and their mono- chlor-, brom- and nitro- derivatives have been observed by Schaarschmidt and Kasai [39] to change from a yellowish-white to a brown color on exposure to a mercury arc. Various ones exhibit the following order of decreasing sensitiveness: 4-chloro-1-methylanthraquinone, 2-methylanthraquinone, 1-methylanthraquinone, 3-chloro-2-methylanthraquinone, 1-chloro-2-methylanthraquinone, 1-chloro-2-bromomethylanthraquinone, 1,3-dimethylanthraquinone. (1,3-Dimethylbenzophenone was not appreciably affected when similarly treated.) The change, at least in the first of these, occurs in a vacuum or in nitrogen as well as when air is present. The change is therefore considered to consist in a transformation into a highly colored quinonoid modification which is not completely reconverted into the original form when rapidly crystallized from alcohol.

Eckert [40] has noted that when 2-methylanthraquinone in acetic acid is exposed for a long time to sunlight with free access of air, the solution becomes increasingly turbid with formation of, chiefly, 2 anthraquinonecarboxylic acid, together with an alkali-insoluble product, which is very probably 2,2′-dianthraquinonylethane. Other derivatives of 2-methylanthraquinone and of 1-methylanthraquinone react in the same way, although less markedly. The oxidation of the former proceeds much more slowly or not at all in other solvents such as toluene, which is itself oxidized to benzoic acid.

He also observed [41] that a solution of potassium anthraquinone-1-sulfonate in hydrochloric acid (1:1) on exposure to light evolves chlorine and yields 1-chloroanthraquinone. Potassium anthraquinone-1,8-disulfonate similarly forms 1,8-dichloroanthraquinone, but the 1,5-disulfonate yields mainly the 1-chloro-5-sulfonate and only little of the 1,5-dichloroanthraquinone. Sodium anthraquinone-2,6-disulfonate affords little 2,6-dichloroanthraquinone and much sodium 2-chloroanthraquinone-6-sulfonate. Anthraquinone-2,7-disulfonic acid yields only products soluble in water. It was possible to isolate 2-chloroanthraquinone-7-sulfonic acid and an isomer. The nitroanthraquinonesulfonic acids react with greater difficulty. 5-, 8-, and 6-Chloro-1-nitroanthraquinones have been obtained from the corresponding sulfonic acids. The bromanthraquinones could not be isolated after exposing solutions of anthraquinone-1 (and -2) sulfonates in hydrobromic acid, although bromine was readily liberated. Eckert and Hampel [42] find that 4,4′-dimethoxy-*meso*-benzbianthrone in chlorobenzene is converted by long exposure to sunlight into naphthobianthrone.

On exposure to light, 3,6′-diacetoxydianthraquinone in benzene solution is slowly changed into diacetoxynaphthadianthrone.[43] A solution of 3,6′-dihydroxydianthraquinone in alcohol on exposure to light deposited crystals which on acetylation gave diacetoxynaphthadianthrone and a little diacetoxyhelianthrone. When an acetone solution of dimethoxydianthrone is evaporated in daylight, the solute becomes rapidly converted into dimethoxynaphthadianthrone and dimethoxyhelianthrone.

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[38] For absorption data, see, Hayashi, M., Kawasaki, K., and Nakayama, A., *J. Soc Chem. Ind. Japan*, **36**, *Suppl. binding*, 123 (1933); Asahina, Y., and Fujikawa, F., *Ber.*, **68B**, 1558 (1935); Jones, D. C. R., and Mason, F. A., *J. Chem. Soc.*, 1813 (1934); Hayashi, M., and Nakayama, A., *J. Soc. Chem. Ind. Japan*, **37**, *Suppl. binding* 238, 239 (1934); Marriott, G. J., and Robinson, R., *J. Chem. Soc.*, 1631 (1934); Castille, A., *Bull. acad. roy. med. Belg.*, **8**, 74 (1928); Clar, E., *Ber.*, **65B**, 503 (1932).

[39] Schaarschmidt, A., and Kasai, K., *Ber.*, **57B**, 1671 (1924).

[40] Eckert, A., *Ber.*, **58B**, 313 (1925).

[41] Eckert, A., *Ber.*, **60B**, 1691 (1927).

[42] Eckert, A., and Hampel, J., *Ber.*, **60B**, 1693 (1927).

[43] Perkin, A. G., and Yoda, G., *J. Chem. Soc.*, **127**, 1884 (1925).

Weber[44] observed that the resulting dyes were off-color when textiles which had been dipped in solutions of the leuco- compounds of certain halogen-containing anthraquinone and indigoid dyes were exposed to sunlight before oxidation. He regarded this as due to dehalogenation, since the color produced in each case corresponded to that of the halogen-free dye. This suggested a method for the removal of halogen from compounds of the anthraquinone series. Goldstein and Gardner[45] applied it with success in a number of cases. The effect is due to visible rather than to ultraviolet light. 1- and 2-Chloro-, 1- and 2-bromo-, and 1-chloro-4-hydroxyanthraquinone were exposed in alkaline sodium hydrosulfite solutions to a 500-watt Eastman "Floodlight" with exclusion of air. The anthrahydroquinones were then oxidized by air and the amount of dehalogenation calculated from the halogen content of the crude product. The final product from each of the halogen anthraquinones was identified as anthraquinone and that from 1-chloro-4-hydroxylanthraquinone as α-hydroxyanthraquinone. The α-halogen is much more readily removed than β-halogen, and bromine more readily than chlorine.

Anthrahydroquinol-α-carboxylic lactones in alkaline, acid or neutral solutions are sensitive to air, especially in benzene or xylene in light.[46] The 2-methyl derivative of anthrahydroquinol-1-carboxylic lactone gave chiefly with typical oxidizing agents 2,2′-dimethyl-9,9′-dihydroxyl-1,1′-dicarboxylic dilactone. Aqueous and especially alcoholic alkalies dissociate the latter with formation of an olive-green solution containing the salts of the anthraquinone and the anthrahydroquinol acids apparently in quinhydrone-like combination. Probably the primary step is a dissociation into an anthoxyl radical with univalent oxygen. Exposure in acetic acid to ultraviolet light, and heating in certain organic solvents, apparently also brings about a similar dissociation.

Much has been written in regard to the use of anthraquinone derivatives in facilitating photochemical oxidations of a wide variety of organic compounds. The anthraquinone in light acts as an oxygen carrier, the carbonyl groups being reduced to carbinols. These regenerate the anthraquinone on shaking with air. When dextrose is the oxygen acceptor, this reaction occurs also in the dark.[47] Other quinones (benzoquinone, naththoquinone, acridone) xanthone and benzophenone are less effective. Anthraquinone is unable to oxidize naphthalene in acetic acid to phthalic acid.

Kreidl[48] uses as catalysts, in effecting such oxidation reactions, ring-system hydrocarbons containing at least three condensed nuclei, such as anthracene; substitution products of such hydrocarbons; substances of quinonoid type, with a ring system containing at least three condensed nuclei and of a lower state of oxidation with respect to at least one of the quinonoid carbon atoms than corresponds to anthraquinone; substitution products of such substances; or hydrogenated products of hydrocarbons with a ring system containing at least three condensed nuclei or their substitution products. Nozicka[49] effected such photochemical oxidation processes in the presence of a catalyst of the anthraquinone type in conjunction with one or more auxiliary catalysts, such as sodium or potassium hydroxide, active carbon, inorganic gels or oxides of copper, bismuth, iron, vanadium or silver. Illustrative reactions[50] are the oxidation of toluene to benzoic acid, of paraffin oil to fatty acids, of lepidine to cinchoninic acid, etc.[51]

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[44] Weber, A. E., *Dyestuffs*, **33**, 1 (1933); *Am. Dyestuff Reptr.*, **22**, 157 (1933); *Chem. Abs.*, **27**, 3336 (1933); *Brit. Chem. Abs.*, **1933B**, 344.

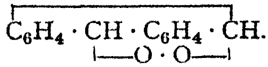
[45] Goldstein, A. E., and Gardner, J. H., *J. Am. Chem Soc.*, **56**, 2130 (1934).

[46] Scholl, R., and Renner, F., *Ber.*, **62B**, 1278 (1929).

[47] Pfeilsticker, K., *Biochem. Z.*, **199**, 8 (1928).

[48] Kreidl, I., U. S. P. 1,971,042, Aug. 21, 1934; *Chem. Abs.*, **28**, 6066 (1934).

[49] Nozicka, F., German P. 526,195, October 27, 1929; *Chem. Abs.*, **25**, 4184 (1931).

Oxidation of Anthracene. Hibberd[52] states that anthracene exposed to daylight or to light of the Fade-Ometer (See Chapter 30) becomes yellow or brown and gives a positive reaction for anthraquinone. Dufraisse and Gérard[53] state that under certain conditions anthracene combines with oxygen to form a colorless, crystalline photo-oxide of the structure  $\underset{O \cdot O}{\overline{C_6H_4 \cdot CH \cdot C_6H_4 \cdot CH}}$. This is stable at ordinary temperatures, but at 120°C. decomposes explosively without evolution of oxygen. It can be titrated with potassium iodide, which reduces it to anthranol or oxanthrol, but isomerization and subsequent oxidation to other products also occur. The photo-oxide resembles oxanthrone in state of oxidation and in giving, with hydrochloric acid and hydrobromic acid, 10-chloro- and bromoanthrone, respectively. 9-Phenyl-10-iodoanthracene is irregularly photo-oxidizable. 9-Phenyl-10-carboxyanthracene and its methyl ester are also photo-oxidizable, but the carboxyl group apparently hinders the addition of oxygen. The photo-oxide of 9-phenylanthracene can be obtained in only 30 per cent yield.[54]

Although the 9,10-diarylanthracenes form photo-oxides that dissociate on heating, that of anthracene explodes at 120°C., and that of 9-phenylanthracene decomposes at 155° with emission of about 12 per cent of oxygen.[55] 10-Methyl- and 10-ethyl-9-phenylanthracene photoöxides behave more like 9-phenylanthracene than like the diaryl compounds, decomposing at 170° and 200° with evolution of 20 and 34 per cent of oxygen, respectively.

To determine whether the reason that anthracene photo-oxide does not liberate all its oxygen on pyrolysis while the corresponding diphenylanthracene photo-oxide liberates 95 per cent of its oxygen[56] might be the greater oxidizability of hydrogen as compared with the phenyl group, Dufraisse and Priou[57] studied the *meso*-dimethoxy-photo-oxide in the expectation that the methoxyl radical would be less oxidizable than the phenyl. They found, however, that this explanation does not hold, since the compound is unstable in light, especially when in solution. It melts at 145°C., with decomposition, leaving a residue of anthraquinone. Willemart[58] found 9,10-di-α-naphthylanthracene, as well as the di-β-naphthyl compound, when exposed to sunlight in the presence of air to yield photoöxides. The latter heated at 180-200°C. lose oxygen and regenerate the hydrocarbons.[59]

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[50] French P. 702,183, Aug. 27, 1930, to Vereinigte Chemische Fabriken Kreidl Heller & Co.; *Chem. Abs.*, **25**, 3919 (1931); Austrian P. 151,652, Nov. 25, 1937; *Chem. Abs.*, **32**, 2029 (1938).

[51] See also German P. 624,964, Feb. 1, 1936, to Kreidl, Heller & Co.; French P. 739,711, July 6, 1932; German P. 536,195, Oct. 27, 1929.

[52] Hibbert, E., *J. Soc. Dyers Colourists,* **44,** 377 (1928); *Brit. Chem. Abs.*, **1929B,** 88.

[53] Dufraisse, C., and Gérard, M., *Compt. rend.*, **201,** 428 (1935); **202,** 1859 (1936). For a more detailed study of the influence of solvents on photopolymerization and photoöxidation, which have as common intermediate an unstable dimer, see Dufraisse, C., and Gérard, M., *Bull. soc. chim*, **4,** 2052 (1937).

[54] Dufraisse, C., Velluz, L., and Velluz, Mme., *Compt. rend.*, **203,** 327 (1936). Since phenanthrene and naphthalene structures do not form photo-oxides, this is a phenomenon different from the accelerated photo-oxidation of numerous unsaturated compounds. Dufraisse, C., and Priou, R, *Bull. soc. chim.*, **5,** 611 (1938)

[55] Willemart, A., *Compt rend.*, **203,** 1372 (1936); *Bull. soc. chim.*, **4,** 357 (1937).

[56] Dufraisse, C., and LeBras, J., *Bull. soc. chim.*, **4,** 349 (1937); Dufraisse, C., Velluz, L., and Velluz, Mme., *Ibid.*, **4,** 1260 (1937); Velluz, L, and Velluz, Mme., *Bull. soc chim*, **5,** 192, 606, 1073 (1938); *Chem. Abs.*, **32,** 3379 (1938).

[57] Dufraisse, C., and Priou, R., *Compt. rend*, **204,** 127 (1937).

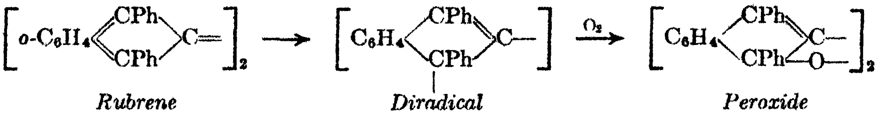
[58] Willemart, A., *Compt. rend.*, **201,** 1201 (1935).

[59] See also Willemart, A., *Compt. rend.*, **202,** 140 (1936); *Bull. soc. chim*, **4,** 510 (1937) for the tolyl derivatives.

9-Methyl (or ethyl)-anthracene polymerizes when irradiated. At the melting points of the polymers, the original hydrocarbons are regenerated, but under certain conditions photo-oxides may be obtained which do not evolve oxygen on heating. Dimethyl (9,10)-derivatives of 9-phenylanthracene do not polymerize.[60]

Acridine and 9-phenylacridine give no light-stable photo-oxides.[61]

Naphthacenes. The red hydrocarbon rubrene, $C_{42}H_{28}$, (tetraphenyl rubene) forms a peroxide when its benzene solution containing dissolved oxygen is exposed *to visible or ultraviolet light; no oxidation occurs in darkness.*[62] The peroxide is stable in solution, colorless and has a molecular weight of 561. Schönberg[63] believes light converts rubrene into an activated diradical form, which adds oxygen to form the peroxide.



The presence of hydroquinol and pyrocatechol and their methyl ethers retards the reaction. Dissociation of the peroxide into rubrene is accompanied by the emission of light. If a benzene solution of the brown form (which owes its color to the presence of an impurity and is really yellow) is exposed to sunlight and then heated to 80°C., the solution becomes luminous. Irradiation destroys the impurity, but the solution can again be activated by sunlight. When in the solid state, the yellow form is luminous after exposure to sunlight, but it is not luminous in solution.

The quantum efficiency of the formation of the peroxide of rubrene rises to unity at concentrations greater than 0.01 molar, and is independent of wave-length between 3660 and 5460A.[64] Bowen and Steadman believe the reaction to depend on termolecular collisions between an activated and a normal rubrene molecule and an oxygen molecule.

The mechanism of the reaction has been the subject of recent discussion.[65] Schumacher believes an excited rubrene molecule R^- incapable of forming a stable RO_2 molecule by collision with an oxygen molecule, unless it has previously collided with another R molecule to give a long-lived R^* molecule which can form a stable oxide. Another possibility, applicable to the results at low oxygen pressures, is for an R^- molecule to form with oxygen an unstable RO_2 molecule which can be stabilized by collision with another R molecule. Neither excited oxygen molecules nor long-lived excited R molecules are believed to play an important part in the reaction. Gaffron found that at small concentrations the oxygen pressure affects the quantum yield. From data on the quantum yield at small oxygen pressures, he concluded that there must be, in addition to the ordinary, short-lived, active form of rubrene, another comparatively long-lived (10^{-2} to 10^{-1} second) active form during the life of which every collision leads to reaction. Schumacher has finally suggested that Gaffron may not have measured the pure rubrene oxidation. The discussion of the mechanisms, too intricate to be given here, is of some significance for the theory of photosensitized processes, since Gaffron views the oxidation, at least in the case of high rubrene concentrations, as what may be called a self-sensitized process.

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[60] Willemart, A., *Compt. rend*, **205,** 866, 993 (1937); *Bull. soc. chim.,* **5,** 556 (1938); *Chem. Abs.,* **32,** 4976 (1938). For 9-alkyl-10-phenyl-anthracenes, see *Bull soc. chim.,* **4,** 1447 (1937).

[61] Dufraisse, C, and Houpillart, J., *Bull. soc. chim*, **5,** 626 (1938).

[62] Moureu, C., Dufraisse, C., and Lotte, P., *Compt. rend.,* **190,** 148 (1930); Moureu, C., Dufraisse, C., and Butler, C., *Ibid.,* **183,** 101 (1926).

[63] Schönberg, A., *Ber.,* **67B,** 633 (1934).

[64] Bowen, E. J., and Steadman, F., *J. Chem. Soc.,* 1098 (1934).

[65] Gaffron, H., *Biochem. Z*, **264,** 251 (1933); Schumacher, H. J., *Z. Elektrochem.,* **42,** 522 (1936); Koblitz, W., and Schumacher, H. J., *Z. physik. Chem.,* **B35,** 11 (1937); *Brit. Chem. Abs.,* **A,** I, 255 (1937); Gaffron, H., *Z. physik. Chem.,* **B37,** 437 (1937); *Brit. Chem. Abs.,* **A,** I, 40 (1938); Schumacher, H. J., *Z. physik. Chem.,* **B37,** 462 (1937).

The relative rates of oxidation of tetraphenylrubrene in 1 : 10,000 dilution in ten organic solvents in the light of a carbon arc have been determined by Dufraisse and Badoche,[66] that in benzene being taken as unity. The highest value, 9, was obtained in carbon disulfide. That in nitrobenzene was 0.10. These different rates seem to be connected with the ability of the solvents to accept oxygen. In the case of nitrobenzene, however, it is probably related to the ability of the solvent to extinguish fluorescence. The high rate observed in carbon disulfide is greatly reduced by the addition of ether. Acetone had little effect on the rate in nitrobenzene. In general, the oxidation is the more rapid the more nearly the absorption maximum in the given solvent approaches the red, but definite relations could not be deduced.

It has been suggested that pure oxygen can be extracted from air by way of the dissociable photo-oxide of rubrene or of *meso*-diphenylanthracene.[67]

The compound formed by exposure of a chlorophyll solution to light in the presence of an acceptor [68] has a diradical character similar to that obtained in the case of rubrene.[69]

A review of the literature on the synthesis and photochemical properties of the naphthacenes (a term used to replace rubrenes) has been given by Dufraisse and Horclois.[70] Naphthacene forms a photo-oxide, $C_{18}H_{12}O_2$, colorless needles, which gives no oxygen on decomposition. Diphenyl-9-10-naphthacene gives a photo-oxide, $C_{30}H_{20}O_2$, which liberates iodine from potassium iodide, but melts at 160° without giving oxygen. 1,2,3,4-Tetrahydro-9,10-diphenylnaphthacene gives a photo-oxide, $C_{30}H_{24}O_2$, which regenerates the original hydrocarbon and liberates 80 per cent of its oxygen at 200°C. The presence of two hydrogen atoms in the 1,1′-positions in rubrenes suppresses the reversibility of absorption of oxygen.[71]

1,1′-*Bis*(*p*-tolyl)-3,3′-diphenyl-5,5′-dimethylrubrene, $C_{46}H_{36}$, forms red solutions which are decolorized by light in the presence of air with the formation of a peroxide.[72] Dufraisse and Loury [73] found ethyl-1,1′-diphenylrubrene-3,3′-dicarboxylate to form a photo-oxide which at 190°C. loses a little oxygen and much carbon dioxide. Solutions of 1,1,3′-triphenylrubrene-3-carboxylate in alcohol are moderately rapidly decolorized by sunlight, but the corresponding acid is much more stable.[74] The residues from the resulting solution are complex and, when heated, evolve mainly carbon dioxide mixed with from 3.7 to 6.0 per cent of the amount of oxygen to be expected from a peroxide. In sunlight, a solution of 0.0678 gm. of 9,10,11-triphenylnaphthacene (triphenylrubrene) in 2.5 cc. of benzene absorbed one mole of oxygen in an hour and became colorless. Larger-scale work led to the isolation of the photo-oxide, $C_{36}H_{24}O_2.C_6H_6$ which, on heating under various conditions, liberated from 6 to 15 per cent of oxygen. It is probably an internal 11,12-dioxytriphenylnaphthacene.[75]

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[66] Dufraisse, C., and Badoche, M., *Compt. rend.*, **200**, 1103 (1935).

[67] Dufraisse, C., and Le Bras, J., *Bull. soc. chim.*, **4**, 349 (1937).

[68] Gaffron, H., *Biochem. Z.*, **264**, 251 (1933); *Chem. Abs.*, **27**, 5763 (1933).

[69] Schönberg, A., *Annalen*, **518**, 299 (1935); Müller, E., and Müller-Rodloff, I., *Annalen*, **517**, 134 (1935); *Chem. Abs.*, **29**, 5320 (1935).

[70] Dufraisse, C., and Horclois, R., *Bull. soc. chim.*, **3**, 1872, 1880 (1936); *Brit. Chem. Abs.*, **A**, 1499 (1936).

[71] Dufraisse, C., and Loury, M., *Compt. rend.*, **200**, 1673 (1935); *Chem. Abs.*, **29**, 5108 (1935).

[72] Dufraisse, C., and Monier, J. A., Jr., *Compt. rend.*, **196**, 1327 (1933); see also Dufraisse, C., and Chovin, P., *Compt. rend.*, **197**, 1127 (1933).

[73] Dufraisse, C., and Loury, M., *Compt. rend.*, **199**, 957 (1934).

Hexabromotetraphenylrubrene in benzene in direct sunlight forms colorless crystals of the peroxide, which decomposes to yield 76 per cent of the theoretical amount of oxygen at 150°C. in thirty to forty-five minutes or in fifteen minutes at 200°C.[76]

OTHER HYDROCARBONS

Chrysogen, the yellow impurity occurring with anthracene, and probably a hydrocarbon, is easily destroyed by exposure of its xylene solution to light. It apparently undergoes polymerization to a colorless substance in a manner similar to anthracene.[77]

In the production of skin cancers in mice by the repeated application of a 1-per cent solution of 1,2-benzopyrene in benzene, sunlight exerts an accelerating influence.[78]

A benzene solution of benzaldehyde and acenaphthene, exposed to sunlight for two years, yielded[79] two polymers of benzaldehyde, one previously observed by Ciamician and Silber,[80] and the other a trimer previously obtained by Mascarelli,[81] a compound corresponding to the addition of a molecule each of acenaphthene and benzaldehyde less a molecule of hydrogen. In addition, there were formed stilbene, isostilbene and resinous material.

The autoxidation of decalin is accelerated by ultraviolet, according to Castiglioni.[82] The exposure of an alcoholic solution of 5-tetraleneacetic acid to the radiation of a quartz mercury lamp yields dihydronaphthylacetic acid.[83]

According to Goldschmidt and Reichel,[84] the yellow product obtained together with fluorenone and $\Delta^{9,9'}$-di-fluorenylene by the atmospheric oxidation of 9-aminofluorene in sunlight, or ultraviolet light, can also be formed with loss of ammonia when oxygen is passed over the base at 75 to 80°C. in darkness. It must be tetrafluorenylhydrazine, its colored solutions containing the radical $(C_{13}H_9)_2N^-$. Optically active, colorless, 3-methoxy-9-phenylfluorene-9-thioglycollic acid turns first yellow and then orange in ultraviolet light. This change occurs also in the case of solutions of phenylfluorenylcarbinols, but the 9-phenylfluorenes are insensitive to light. Racemization is the principal effect of light.[85]

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[74] Badoche, M., *Compt. rend.*, **198**, 662, 1515 (1934); **200**, 750 (1935).

[75] Badoche, M., *Bull. soc. chim.*, **3**, 2040 (1936).

[76] Dufraisse, C., and Velluz, L., *Bull. soc. chim.*, **3**, 254 (1936).

[77] Capper, N. S., and Marsh, J. K., *J. Am. Chem. Soc.*, **47**, 2848 (1925). For absorption data on phenanthrene see Goldschmidt, S., and Graef, F., *Ber.*, **61B**, 1858 (1928); Titeica, R., *Bul. soc. romane fiz.*, **35**, 149 (1933); *Chem. Abs.*, **28**, 1618 (1934); Clar, F., and Lombardi, L., *Ber.*, **65B**, 1411 (1932); Askew, F. A., *J. Chem. Soc.*, 509 (1935). It is not autoxidizable in light. Benrath, A., and v. Meyer, A., *Chem. Abs.*, **7**, 352 (1913).

[78] Maisin, J., and de Jonghe, A., *Compt. rend. soc. biol.*, **117**, 111 (1934).

[79] De Fazi, R., *Atti accad. Lincei*, **9**, 1004 (1929); *Chem. Abs.*, **24**, 362 (1930).

[80] Ciamician, G., and Silber, P., *Chem. Abs.*, **4**, 1619 (1910).

[81] Mascarelli, L., *R. Accad. Lincei*, **15**, II, 375 (1906).

[82] Castiglioni, A., *Gazz. chim. ital.*, **64**, 465 (1934); *Brit. Chem. Abs.*, **A**, 1184 (1934); Moureu, C., Dufraisse, C., and Chaux, R., *Chem. Abs.*, **21**, 1914 (1927). For the irradiation of squalene, see *J. Soc. Chem. Ind.*, 181 (1926).

[83] Schroeter, G., *Ber.*, **58**, 713 (1925).

[84] Goldschmidt, S., and Reichel, L., *Annalen*, **456**, 152 (1927).

Crude synthetic perylene may be purified by exposing it to a quartz mercury arc.[86] Ether solutions of crude coal-tar show increased ultraviolet transmission after having been similarly irradiated.[87]

On illumination of a cyclohexane solution of carotene, the pressure of oxygen above it in a closed vessel drops initially and reaches a constant value in about three hours. If all or part of the oxygen is then pumped out in the dark, on re-illumination, a pressure rise is observed, indicating an equilibrium between carotene, its oxide and oxygen. But in the case of an octane solution, the oxygen pressure decreases linearly with time without reaching a minimum value.[88]

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[85] Lifschitz, I., *Rec. trav. chim.*, **54**, 397 (1935); *Chem. Abs.*, **29**, 5437 (1935).

[86] Postovskii, I. Y., and Bednyagina, N. P., *J. Gen. Chem. (U. S.S. R.)*, **7**, 2929 (1937); *Chem. Abs.*, **32**, 5396 (1938).

[87] Herrick, J. F., and Sheard, C., *Proc. Soc. Exptl. Biol. Med.*, **26**, 33 (1928).

[88] Baur, E., *Helv. Chim. Acta*, **20**, 402 (1937).

Chapter 27

Compounds with Heterocyclic Rings

OXYGEN-CONTAINING RINGS

Essential Oils. The spontaneous transformation of solutions of various odorous substances into a colloidal state by exposure to light has been investigated by Zwaardemaker and Hogewind.[1] In the case of several substances the change occurred only in the presence of ultraviolet light and the resulting colloidal particles were negatively charged. Among the substances studied were eugenol, cresol, guaiacol, carvacrol, citral, cumidine, thymol and hypnone.

A sample of dark yellow distilled lavender oil was found by Quilico[2] to be progressively decolorized by exposure to ultraviolet rays without losing its original fragrance. After one hour, 20 cc. were colorimetrically equivalent to only 19.5 cc. This became 11.5 cc. after 7, 2.5 after 14 and 0.5 cc. color equivalent after 21 hours. Eucalyptus oil was decolorized slightly more rapidly. It was suggested that the formation of oxygenized products caused the slightly lower results in the lavender oil. The essential oil of *Monarda fistulosa* behaves in the opposite manner, becoming brown when exposed to light, according to Badzynski.[3]

Absorption data on a series of oils have been given by Morton[4] and may serve as an aid in the identification of constituents. Maxima are found at 3070 and 2370A (wintergreen), 2810 and 2435A (almond), 2810A (clove), 2770A (thyme), 2860A (cinnamon and cassia), 2850 and 2330A (sassafras), 3110A (lemon), 2380A (mustard), 2320A (cade). Wormseed and mace oils show but little selective absorption. Previous observations on the use of ultraviolet spectrograms in the identification of essential oils were due to Boyer.[5]

It is well known that good quality peppermint oil when used in flavoring certain candies or sugar preparations, such as ordinary mint tablets, loses its fine flavor on long standing. In the laboratory of the senior author, a number of samples of such tablets were exposed to the action of ultraviolet in order to test the stability of certain mint oils in the manufacture of confections. It was found that a few hours' exposure afforded approximately the same aging effect as standing on the shelves for a period of several months. The procedure appears to be a ready method of testing materials of this class to determine quickly their keeping qualities.

It is said that the oxidation of Russian turpentine is more rapid in sunlight than in artificial light,[6] due to its ultraviolet rays. Jorissen and Vollgraff[7] claim that the autoxidation of pinene under the influence of the rays from a Uviol lamp increases the electric conductivity of oxygen.

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[1] Zwaardemaker, H., and Hogewind, F., *Proc. Akad. K. Wetensch. Amsterdam*, **21**, 131 (1918); *J. Chem. Soc.*, **116**, ii, 14 (1919).

[2] Quilico, A., *Rivista ital. essenze profumi*, **10**, 148 (1928); *Chem. Abs.*, **23**, 2784 (1929).

[3] Badzynski, S., *Wiadomoscki Farm.*, **60**, 689 (1933); *Chem. Abs.*, **28**, 1815 (1934).

[4] Morton, R. A., *Perfumer and Essential Oil Record*, **20**, 258 (1929). See also Harvey, E. H., *J. Am. Pharm. Assoc.*, **19**, 1173 (1930); *Chem. Abs.*, **25**, 5850 (1931); van Os, D., and Dykstra, K., *J. pharm. chim.*, **25**, 437, 485 (1937).

[5] Boyer, J., *Am. Perfumer*, **17**, 389 (1922).

[6] Korotkov, K. N., *Mem. Belloruss. State Acad. Agr.*, **5**, 16 (1927); *Brit. Chem. Abs.*, **B**, 650 (1929); *Lesokhim. Prom.*, **4**, No. 11, 6 (1935); *Chem. Abs.*, **30**, 8658 (1936).

[7] Jorissen, W. P., and Vollgraff, J. A., *Chem. Weekblad*, **12**, 93 (1915); *J. Chem. Soc.*, **108**(ii). 80 (1915).

Pinene itself on exposure to ultraviolet rays gives acetylene, ethylene and hydrogen, the liquid containing some isoprene.[8]

Dedichen and Halse[9] expose raw turpentine oil to the action of ultraviolet rays while subjecting it to the action of air or oxygen. The oil is then treated with iron chloride to refine and deodorize it, and obtain a mixture of α- and β-pinenes containing dextrorotatory β-pinenes.

Selenious acid or anhydride may react, under pressure and in the presence of ultraviolet light, with compounds containing the group $CH{=}CHCH_2$, eventually yielding unsaturated α-β-diketones. As starting materials, 1-methane, α-pinene, β-pinene, dipentene-3-methene and eugenol may be employed.[10]

When light acts on mixtures of acetone with some terpene alcohols the formation of pinacols can be confirmed. No other derivatives could be isolated by Scagliarini and Saladini.[11] Terpinol hydrate did not condense with acetone. However, 79.7 gm. of acetone and 53 gm. of geraniol after thirteen months in sunlight gave 63 gm. of acetone, 32 gm. of geraniol and a yellowish residue, boiling at 208-10°C. and composed of $(CH_3)_2C{=}CHCH_2CH_2.C.CH_3{=}CHCH(OH)C(OH)(CH_3)_2$. From a similarly exposed mixture of acetone and menthol about 90 per cent of the original compounds and an analogous condensation product were recovered. Similar results were attained with borneol and acetone.

When air is passed through isoeugenol in which is immersed a lamp emitting ultraviolet rays, vanillin is formed.[12] The rate of oxidation depends upon the penetrating power of the rays. This in turn depends upon the clearness of the isoeugenol and makes necessary the use of the more expensive distilled isoeugenol. Even with this, the oil darkens in a couple of hours and the rate of oxidation rapidly decreases. Another difficulty attending the commercial application of the process is the fact that the rapid circulation of air through the solution as employed in practice caused a considerable loss of isoeugenol by vaporization. In one run in which 30,000 cu. ft. of air were circulated per hour through 800 lbs. of isoeugenol, the loss amounted to about 80 lbs. in eight hours. It was presumed that the oxidation of the isoeugenol was due to the action of ozone formed in the circulated air by the ultraviolet rays. Genthe and Co.[13] claim that the yield of vanillin may reach 95 per cent.

Scagliarini and Saladini[14] exposed 4.7 gm. of fenchone and 4 gm. of toluene in 100 cc. of water in 5-liter flasks full of oxygen to sunlight for nearly a year. Much carbon dioxide was formed and 9.3 gm. of benzoic acid could be separated from eight such flasks in addition to some acetic acid. Similar experiments with fenchone and ethyl alcohol in water gave much carbon dioxide, considerable acetic and some oxalic acids and an undetermined compound with 49.39 per cent carbon and 11.32 per cent of hydrogen. Neither fenchone nor alcohol could be oxidized separately and no easily oxidizable addition product of the two could be detected.

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[8] Urbain, E., and Scal, C., *Compt. rend.*, **168**, 887 (1919).

[9] Dedichen, H., and Halse, O. M., U. S. P. 1,253,793, Jan. 15, 1918; *Chem. Abs.*, **12**, 770 (1918).

[10] Schwenk, E., and Borgwardt, E., German P. 608,136, Jan. 17, 1935; French P. 751,807, Sept. 11, 1933; *Chem. Abs.*, **29**, 6246 (1935).

[11] Scagliarini, G., and Saladini, G., *Gazz. chim. ital.*, **53**, 135 (1923); *Chem. Abs.*, **17**, 2281 (1923).

[12] Wood, B. G., *Chem. & Met. Eng.*, **28**, 399 (1923).

[13] Genthe and Co., German P. 224,071.

[14] Scagliarini, G., and Saladini, G., *Gazz. chim. ital.*, **53**, 135 (1923); *Chem. Abs.*, **17**, 2281 (1923).

Similar experiments with pinene and oxalic acid gave carbon dioxide, tar, much unchanged pinene and oxalic acid and some acetic acid.[15]

β-Caryophyllene nitrosite in solution evolves nitrogen when exposed to red light.[16] Its absorption is confined to a narrow band with its head at about 6800A.[17] The quantum yield is, for the nitrogen formed, 0.38 and for the disappearance of the nitrosite as determined optically, 1.37.[18] These values were obtained with oxygen excluded. In its presence, the latter value was higher, 2.9. The gas evolved in the absence of oxygen contained 86.1 per cent nitrogen and 13.9 per cent of nitrogen trioxide.

That nitropiperonal becomes brown on exposure to sunlight was noted by Ekeley and Klemme.[19] Since the isomeric nitropiperonal isolated from a Kahlbaum product is brownish-yellow, it was thought that it might have been produced from the ordinary form by a light reaction. When, however, ordinary nitropiperonal was exposed in thin layers to sunlight and to ultraviolet light, the brown product yielded on recrystallization only nitropiperonal and a tarry brown residue but no isomer.

Piperitone in aqueous acetic acid or alcohol yields (in the light of a quartz mercury arc) needles of a dimer which can be separated into three fractions of the same composition and molecular weight, but which differ in form, melting point and ability to form a semicarbazone. Carvone seems also to form two dimers under these conditions. In sunlight, however, both piperitone and carvone each form only one dimer.[20]

Pimpinellin when subjected in a thin layer to diffused sunlight for two and a half months or to ultraviolet light for 16 hours, and then extracted with ethyl acetate, yields a dimer melting at 237-8°C. When heated four hours on a water-bath with 5-per cent sodium hydroxide this dimer gives furan-2,3-dicarboxylic acid. The action of light upon pimpinellin in cold acetic acid gives a different dimer, melting at 256-7°C., from which the furan derivative could not be isolated after alkaline treatment.[21]

Attempts to isomerize campholic acid by means of ultraviolet light have not been successful [22]; nor does ultraviolet light accelerate the isomeric change of nitrocamphor, or of hydroxymethylene camphor.[23] In the case of aminomethylene-camphor there is a marked acceleration, which ceases when the stimulus is removed. Benzoylcamphor also undergoes isomeric change more rapidly in the presence of radiation, but the acceleration persists after the rays have been withdrawn, possibly because of the liberation of benzoic acid which acts as a powerful catalyst in promoting the isomeric change.

In sunlight, α-naphthylaminocamphor in chloroform forms substituted green compounds with the solvent; the reactions are reversed in darkness. The substance is oxidized in solution in the presence of light, and eventually naphthylamine liberated in the reaction precipitates in the form of hydrochloride.[24] Singh and

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[15] For other early observations of this type see Ciamician, G., and Silber, P., *Atti accad. Lincei*, **22**, II, 470; Suida, H., *Monatsh.*, **33**, 1277 (1912); Benrath, A., and v. Meyer, A., *Chem. Abs.*, **7**, 352 (1913).

[16] Kremers, E., *Pharm. Arch.*, **2**, 273 (1899).

[17] Mitchell, S., *J. Chem. Soc.*, 3238 (1928).

[18] Hoffman, R. M., *J. Am. Chem. Soc.*, **56**, 1894 (1934).

[19] Ekeley, J. B., and Klemme, M. S., *J. Am. Chem. Soc.*, **50**, 2714 (1928).

[20] Treibs, W., *Ber.*, **63B**, 2738 (1930); *Chem. Abs.*, **25**, 1513 (1931).

[21] Wessely, F., and Dinjasky, K., *Monatsh.*, **64**, 131 (1934); *Chem. Abs.*, **28**, 6435 (1934).

[22] Lipp, P., and Reinartz, F., *Helv. Chim. Acta*, **10**, 611 (1927).

[23] Lowry, T. M., and Courtman, H. R., *J. Chem. Soc.*, **103**, 1214 (1913).

[24] Mitra, B. N., *J. Phys. Chem.*, **35**, 2371 (1931); *Chem. Abs.*, **25**, 5350 (1931).

Bhaduri[25] extended the observations of phototropic change to other solvents. It is absent in methyl, ethyl or ethylene iodides. The oxidation reaction yields α-naphthyliminocamphor and the rotatory power is increased. Both reactions are inhibited by water or sodium ethylate.

Diazocamphor prepared from inactive camphor, as well as that prepared from the dextro-compound, are decomposed in benzene solution by light of wave-length 2200-3000A, but visible light has almost no action.[26]

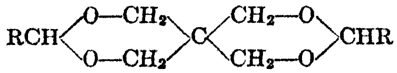
The transformation of santonin into photosantonic acid and isophotosantonic acid proceeds by way of intermediate compounds.[27] Photosantonic acid and probably also isophotosantonic acid are very transparent to ultraviolet rays, but santonin is not. No confirmation could be obtained by Piutti of the reported reconversion of yellow santonin into white on boiling. Any visible alteration of santonin crystals under radiation could not be confirmed.

Other Compounds with Oxygen in Rings. 3-Methylcyclohexenone irradiated by a mercury arc for seventeen hours in dilute methanol gives a saturated dimer melting at 144-5°C. and an unsaturated liquid, oily dimer. The photodimer of 3,5-dimethylcyclohexenone melts at 161-2°C. The mother liquor gives an isomer and an unsaturated substance, boiling at 203-5°C. (17 mm.).[28]

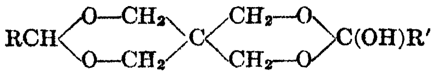
Tănăsescu[29] finds that *bis-o*-nitrobenzalpentaerythrito-1-spiran (I) in the solid state becomes slowly colored in sunlight. The change proceeds more rapidly in solution, especially in benzene. (Compare nitrobenzaldehyde.) Only one of the two nitro groups in I reacts with the formation of a compound II. By alkaline saponification of II. *o*-nitrosobenzoic acid and a product III are formed. That III still contains an unaltered nitro- group is shown by its photochemical behavior,

$R' = C_6H_4NO_2$

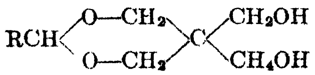
I.



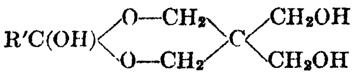
II.



III.



IV.



whereby it is rapidly converted into IV. I rapidly becomes colored on exposure in the solid state to sunshine, the melting point falling in ten days from 166° to 95°C. In ethanol, no crystallizable reaction products can be recovered, but in acetone, ethyl acetate, chloroform, pyridine, and especially benzene, the reaction product is the compound II, of melting point 135°C. In the last-named solvent, the reaction requires only fifteen minutes.

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[25] Singh, B. K., and Bhaduri, B., *Trans. Faraday Soc.*, **27**, 478 (1931); *Chem. Abs.*, **25**, 5627 (1931).

[26] Bredig, G., Mangold, P., and Williams, T. G., *Z. angew. Chem.*, **36**, 456 (1923); *Chem. Abs.*, **17**, 3868 (1923).

[27] Piutti, A., *Atti accad. Lincei*, **22**, ii, 92 (1913).

[28] Treibs, W., *J. prakt. Chem.*, **138**, 299 (1933).

[29] Tănăsescu, I., *Bul. soc. stiinte Cluj*, **2**, 111; *Chem. Abs.*, **19**, 2932 (1925). See also Radulescu, D., *Chem. Abs.*, **18**, 1285, 1286 (1924).

[30] Cornubert, R., Andre, M., de Demo, M., Joly, R., Louis, P., Robinet, P., and Strebel, A., *Bull. soc chim.*, **5**, 513 (1938); *Chem. Abs.*, **32**, 5384 (1938).

Benzylidine derivatives of α-methylcyclohexanone and α-methylcyclopentanone, and of α-isopropylcyclopentanone, undergo oxidation or polymerization on standing. This may be accelerated by ultraviolet light.[80]

4-Methyl-2,6-dianisal-1-cyclohexanone is photosensitive and slowly turns orange-red behind glass. Its pale rose pentabromo-derivative is also photosensitive, turning maroon and violet-red.[81]

Mixtures of indole, various aldehydes and ethyl alcohol, set aside in closed bottles in diffused light for one year and then in sunlight for another year, showed progressive chromatic changes.[82] These were greatest with α-methylindole, less evident with indole and least with scatole. This agrees with the ease of formation of rosindoles from these three compounds. Distilled with steam, the distillate contained unaltered indole, while from the filtered residue the aldehyde was recovered on cooling. In every case there was also recovered from the residue a rosindole. Solutions of diindyl-*m*-methoxy-*p*-hydroxybenzylidene in methanol, ethanol, acetone, chloroform and ethyl acetate are at first colorless, but become intense red on exposure to light and air.

Stobbe and Färber [83] have carried out a series of experiments on the photopolymerization of pure indene. In ultraviolet it resinified.[84]

de Fazi [85] illuminated 2.5 gm. of α-methyl-β-phenylindone in 10 cc. of dry benzene in a quartz test tube with a 1500 c.p. quartz mercury arc for a total of 71 hours during 13 days. Crystals of one form of dimethyldiphenyltruxone separated, white, melting at 307-8°C. From the benzene, unchanged α-methyl-β-phenylindone and the other isomer of the dimethyldiphenyltruxone, yellow, melting at 250-260°, were separated. Each isomer treated with concentrated sulfuric acid gave α-methyl-β-phenylindone. The white isomer is sensitive to light, developing a partially reversible yellow color. In sunlight, the yellow form at the melting point for ten minutes is converted into α-methyl-β-phenylindone. The oxime and phenylhydrazone of α-methyl-β-phenylindone were exposed to ultraviolet light in benzene. A small amount of a new compound, melting at 73-5°C., was obtained, but the oxime and phenylhydrazone of dimethyldiphenyltruxone have not been obtained in this way. From β-phenyl-β′-phenyltruxone irradiated in benzene with ultraviolet for 48 hours a new yellow isomer of β-phenyl-β′-phenyltruxone, melting at 184-5°, was obtained.[86]

The reciprocal reduction and oxidation of ketones and alcohols by light to pinacols and aldehydes occurs also in the case of α,β′-diisoxazole ketone.[87] Ten grams of this compound and 70 cc. of 95-per cent ethanol in a sealed tube exposed to sunlight until the reaction was complete (ten days) yielded 9.7 gm. of α,β′-diisoxazolepinacol, melting 195-6°C. Exposure of the ketone in benzene and in toluene to sunlight led only to traces of reduction products and to unidentified tars. In water, the reaction was very slow, the corresponding acid being formed after six months.

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[81] Poggi, R., and Gottlieb, M., *Gazz. chim. ital.*, **64**, 852 (1934); *Chem. Abs.*, **29**, 2152 (1935).

[82] Mingoia, Q., *Gazz. chim. ital.*, **56**, 781 (1926); *Chem. Abs.*, **21**, 1118 (1927).

[83] Stobbe, H., and Färber, E., *Ber.*, **57**, 1843 (1924).

[84] Gunz, A., and Minguin, J., *Compt. rend.*, **152**, 373 (1911); note Weger, M., and Billmann, A., *Ber.*, **36**, 642 (1903); Ciamician, G., and Silber, P., *Ber.*, **46**, 420 (1913).

[85] de Fazi, R., *Gazz. chim. ital.*, **54**, 996 (1924). Dichlorohydrindones from the chlorination of α-methyl-β-phenylindone slowly lose chlorine in diffused light. De Fazi, R., and Pirrone, F., *Gazz. chim. ital.*, **67**, 128 (1937); *Chem. Abs.*, **31**, 6649 (1937).

[86] See also Stobbe, H., and Zschoch, F., *Ber.*, **60B**, 457 (1927).

[87] Freri, M., *Gazz. chim. ital.*, **63**, 419 (1933); *Chem. Abs.*, **27**, 5327 (1933).

[88] Milas, N., and McAlevy, A., *J. Am. Chem. Soc.*, **56**, 1219 (1934).

Ultraviolet light of wave-lengths in the range 4500 to 3600A accelerates considerably the decomposition of furoperacid (obtained from di-furoyl peroxide) either in the solid state or in solution in glacial acetic acid.[38]

COMPOUNDS CONTAINING NITROGEN

The lower melting form (65.5-66.5°C.) of methyl-4-benzylidene-3-methylhydantoin-1-acetate when exposed to daylight or ultraviolet light in the presence of a trace of iodine is partly converted into the stereoisomer melting at 98.5-99.5°C. and partly into a polymer melting at 276-278°C.[39]

Some decomposition also occurs with formation of benzaldehyde. The higher-melting stereoisomer similarly yields the lower-melting form and the polymer, the change being preceded by an induction period. 4-Benzylidene-3-methylhydantoin-1-acetic acid also exists in two stereoisomeric forms, melting at 186.5-187.5° and 198.5-199.5°C. The former does not yield measurable quantities of other products when exposed to light for five months. The latter is much more rapidly changed, with production of a small proportion of the lower-melting form and a polymer melting at 293-294°C.

Thymine glycol is easily broken down even in neutral solution by daylight or light from a carbon arc. Lactic aldehyde is formed as an intermediate product which isomerizes into acetol. In weakly alkaline solution, thymine glycol yields urea, acetol and carbon dioxide. In the presence of an oxidizing agent, the products are urea, pyruvic acid and carbon dioxide. With hydrochloric acid solutions or in solutions in which the acidity is produced by the growth of sulfur bacteria, a new anhydride of thymine glycol is produced by carbon arc irradiation. A deep red compound which forms in acid thymine glycol solutions is decolorized upon irradiation to a faint yellow, which shows a green fluorescence in ultraviolet light.[40, 41]

3-Methyl-6,7-benzoylene-β,β-benzopyrrole readily forms solvates and its solutions show different colors which are more or less rapidly decolorized by light, especially ultraviolet light.[42]

α-Picoline in benzene in the presence of anthraquinone gave, after five months of exposure to sunlight, 5.3 per cent of picolinic acid and about 10 per cent of a dark resinous substance soluble in normal sodium carbonate, difficultly soluble in twice normal hydrochloric acid, and giving no precipitate in alcohol with picric acid. Of the anthraquinone, 97.5 per cent was recovered unchanged in experiments of John and Behmel.[43]

Pyridine. Freytag and Neudert find,[44] contrary to Berthelot and Gaudechon, that pyridine is changed by ultraviolet radiations of wave-length less than 3000A. The change is marked by a strong yellow color and an increase in density from 0.97827 to 0.98232 in less than five hours. In methyl alcohol a yellow color begins to appear after four minutes and is marked after two hours. In ethyl alcohol it is first seen in five to ten minutes, in acetone in ten minutes, in amyl alcohol in three minutes and in benzene in thirty minutes. Various salts accelerate the appearance of the color and others inhibit it. Inorganic and organic acids also catalyze the reaction, hydrochloric, nitric, malic and citric acids being particularly effective. Bases are inactive. The zinc chloride compound of pyridine is decomposed into its constituents and the pyridine is changed into the colored photopyridine.

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[39] Hahn, D. A., and Evans, J., *J. Am. Chem. Soc.*, **49**, 2877 (1927).

[40] Johnson, T. B., Baudisch, O., and Hoffmann, A., *J. Am. Chem. Soc.*, **54**, 1106 (1932); Bass, L. J., *Ibid.*, **46**, 190 (1924) has discussed the oxidation of thymine in light. See also Baudisch, O., and Davidson, D., *Ber.*, **58B**, 1680 (1925).

[41] For the photosensitivity of various pyrrole ferrocyanides, see Pratesi, P., *Gazz. chim. ital.*, **65**, 658 (1935).

[42] Scholl, R., Böttger, O., and Stix, E., *Ber.*, **67B**, 1922 (1934).

[43] John, H., and Behmel, G., *Ber.*, **66B**, 426 (1933); *Chem. Abs.*, **27**, 3216 (1933).

[44] Freytag, H., and Neudert, W., *J. prakt. Chem.*, **135**, 15 (1932); *Chem. Abs.* **27**, 724 (1933). Freytag has reviewed his extensive investigations, *Phot. Korr.*, **73**, 17, 37, 57 (1937).

Filter paper impregnated with pyridine, its hydrate or alcoholate, is colored yellow by ultraviolet light. Such papers give various colors on the addition of the salts of aromatic amines. Thus α-naphthylamine hydrochloride gives a light brownish-yellow color and the β-isomer a carmine red color. By the use of such papers, aniline hydrochloride may be detected in dilutions of one part in ten thousand. The test may also be adapted to the detection of pyridine in a dilution of 1 : 26,840. Since the photopyridine is sensitive to water, the test papers should be protected from moisture. Although the color reactions of irradiated pyridine with primary amines are not in every case sufficiently definite to identify the amine, they may serve to indicate the class to which it belongs.[45] The color and fluorescence of solutions of photopyridine with each of 21 aromatic sulfonic acids were also given. F-acid does not react, probably because of the hindering effect of the sulfonic acid group in position 7. The colors produced in most of these identification tests are changed to yellow or orange by alkalies, but the original color is restored by acids.

"Photopyridine" can be isolated by treating the pyridine solution with zinc chloride. It is obtained as a syrup, ruby-red in color, which decomposes on heating and evolves the odor of pyridine. With boiling β-naphthylamine hydrochloride, it gives red-brown needles, which yield colorless crystals on heating. *p*-Nitroaniline hydrochloride gives an orange color; the ether solution is reddish orange, with a green fluorescence. "Photopyridine" is not formed in the absence of oxygen, but it is not among the products of reaction of pyridine with ozone or hydrogen peroxide. It gives a violet color with a purple-violet fluorescence with sodium, potassium and calcium hydroxides, but not with sodium carbonate, sodium borate, disodium phosphate or ammonia. It gives aldehyde reactions and evolves ammonia on treatment with alkalies, and may be regarded as the ammonium derivative of the enolic form of glutacondialdehyde, $CHO \cdot (CH{=}CH)_2ONH_4$.[46]

"Photopyridine" is formed by wave-lengths in the region 2540 to 2660A.[47] Various derivatives of pyridine are also affected by the lines 2540 and 2650 and to a smaller extent by 2480 and 2400A.[48] With the exception of *sym*-collidine, the photoproducts of the homologous pyridines are similar to photopyridine in structure. These include 2-, 3- and 4-methyl, 2,4- and 2,6-dimethyl, 2,4,6-trimethyl, 2,3,4,5-tetracarboxyl and 2-aminopyridines. The 3-amino- derivative is most affected at the wave-lengths 3650, 3130 and 3020A. The resulting photoproducts of these pyridines may be identified by the colors they give with β-naphthylamine. The derivative from diethyl collidinedicarboxylate is apparently the same as that from its hydrogen derivative. The photoproducts are in most cases destroyed by diffused or direct sunlight. Certain pyridines irradiated by wave-lengths less than 3000A become yellow to yellow-brown in aqueous or alcoholic solutions although the products may not be aldehydic, the enol-aldehyde being converted into the dialdehyde form which is then resinified by free acid.

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[45] Freytag, H., *J. prakt. Chem.*, **139**, 44 (1933); *Chem. Abs.*, **28**, 1701 (1934); *J. prakt. Chem.*, **136**, 193 (1933); *Chem. Abs.*, **27**, 2449 (1933).

[46] Feigl, F., and Anger, V., *J. prakt. Chem.*, 139, 180, 343 (1934); Freytag, H., *Ber.*, **67B**, 1995 (1934); **69B**, 32 (1935).

[47] Freytag, H., and Hlučka, F., *J. prakt. Chem.*, **136**, 288 (1933); *Chem. Abs.*, **27**, 2687 (1933).

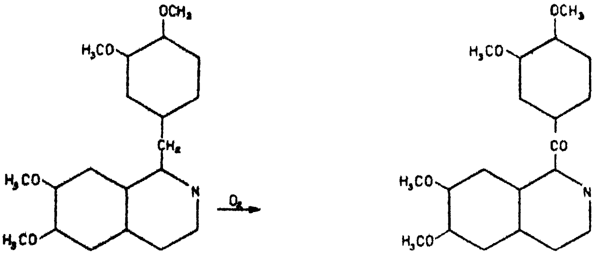
[48] Freytag, H., *J. prakt. Chem.*, **138**, 264 (1933); *Brit. Chem. Abs.* **1933A**, 1304; *Ber.* **69B**, 32 (1936); *Chem. Abs.*, **30**, 2966 (1936) .

A solution of 3-bromo-5-aminopyridine, which assumed an intense color in a short time, gave no aldehyde reactions, but increased in acidity during the first hour and showed the presence of bromide ions. The increasing color possibly acted as an internal filter and slowed the reaction. Oxygen was involved since the coloration began at the surface. The amino- group also may possibly have been attacked. 2-Methyl-5-aminopyridine becomes yellowish-brown but gives no aldehyde reactions and shows no change in pH. Another group of derivatives shows no coloration, but if they contain halogen atoms or esterified carboxyl groups may form halogen ions or free acids on irradiation. Stable toward ultraviolet are 4-chloropicolinic acid and 5-aminopyridine-3-carboxylic acid, which latter has a magnificent blue-violet fluorescence, as well as pyridine-2,3-dicarboxylic acid and coramine, $3\text{-}C_5H_4NCON(C_2H_5)_2$. The chlorine atom is not removed from 4-chloro-2-aminopyridine which becomes colored, possibly because the amino- group is attacked. The rapid brown-yellow coloration of aqueous solutions of 5,6-dichloropyridine-3-aldehyde and the 4,6,2-isomer may be due to attack of the aldehyde group. 4-Iodopyridine-2-carboxylic acid in acid solution liberates hydriodic acid, which is photo-oxidized to iodine and water. Photochemical saponification of diethyl 2,6-dimethylpyridine-3,5-dicarboxylate occurs.

Pure, colorless 2-benzylpyridine, on standing in diffused daylight, becomes yellow-red to brown and shows weak green fluorescence.[49] Filter paper impregnated with a solution of the base (two drops in 10 cc. of alcohol or benzene) turns yellow or brown after one-half to one minute in daylight, gray-brown or greenish after one hour. The product gives a red-purple dye with hot β-naphthylamine solution. With this pyridine derivative, the color of the photoproduct differs somewhat with the wave-lengths used for the irradiation. Longer ones (3650-2700A) give a green discoloration and shorter ones (2650-2480A) a yellow one. The shorter rays produce the usual aldehydic substance and the longer ones, 2-benzoylpyridine with α,β-diphenyl-di-2-pyridylethane.[50]

The reaction has been used in printing fabrics.[51] The fabric is impregnated with a solution of 2-benzylpyridine in 96 per cent alcohol; after evaporation of the alcohol the fabric is covered with a negative plate and exposed to sunlight or ultraviolet rays. When working on cotton, the positive is washed with soap, rinsed and ironed while still moist.

Müller and Dorfman find both pyridine and papaverine, in oxygen-free



Papaverine *Papaveraldine*

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[49] Freytag, H., and Muller, A., *Naturwiss.*, **21**, 720 (1933); *Chem. Abs.*, **28**, 710 (1934).

[50] Müller, A., and Dorfman, M., *J. Am Chem Soc*, **56**, 2787 (1934); *Monatsh.*, **65**, 411 (1935).

[51] Freytag, H., and Müller, A., *Monatschr. Textilind.*, **48**, 239 (1933); *Chem. Abs.*, **28**, 5245 (1934).

water vapor, to be unaffected by light,[52] but 2-benzylpyridine, 2-benzoylpyridine and papaveraldine darken. Papaverine in benzene gives 10 per cent of papaveraldine. In the solid state and in presence of oxygen, papaverine and papaveraldine become brown after several hours in mercury light.

Koller [53] states that 6-styryl-2,4-dichloro-3-cyanopyridine (obtained by heating the 6-methyl compound with benzaldehyde) changes in diffused daylight into a substance melting considerably higher and of double the molecular weight of the original compound. That the polymerization consists in the formation of a cyclobutane ring, with destruction of the ethylene bonds of two molecules of the styryl compound, is indicated by the fact that although the original compound is yellow, the polymer is colorless. The polymer does not react with potassium permanganate in cold acetone. Thinking this polymerization might be a property of stilbazoles in general, Koller exposed a number of other compounds of this type to sunlight and to quartz light but was in no case able to effect dimerization. Cantieni [54] finds that, in the presence of 0.001 to 1 per cent of pyridine, there is evolution of carbon monoxide from fructose solutions when exposed to ultraviolet light. The solution also turns brown. More concentrated pyridine solutions did not produce this effect, which is proposed as the basis of a method for the detection of pyridine in very dilute solutions containing not less than 0.001 per cent. Acetone inhibits the formation of the color, which is less readily formed in solutions containing glucose, galactose, sucrose or lactose. Pure pyridine and aqueous solutions more concentrated than 1 per cent are opaque, and solutions more dilute than 0.001 per cent are transparent to ultraviolet light.

Filter paper soaked in an alcoholic solution of quinoline or lepidine, treated with a 0.05 per cent aqueous solution of pyridine and irradiated, slowly becomes yellow. The reaction may be used for the detection of pyridine in the presence of nicotine, since the latter gives only a grayish color.[55]

Phototropy is exhibited by 2,4,4,6-tetraphenyl-1,4-dihydropyridine, as well as by diphenacyldiphenylmethane, 2,4,4,6-tetraphenyl-3,5-dibenzoyl-tetrahydropyran, all three becoming violet in light and reverting to colorless in the dark.[56]

2-Phenyl-3-methyl-quinoline in benzene solution in the presence of anthraquinone gives (on prolonged exposure to sunlight) in addition to dark resinous matter about 3 per cent of 2-phenylquinoline-3-carboxylic acid.[57] 2-Phenyl-6-methylquinoline yielded 8 per cent of the 6-carboxylic acid.[58] 2-*p*-Tolylquinoline gave no acid and and 37.5 per cent was not attacked, but considerable tar was formed. Conquinine [59] sulfate similarly gave 56.0 per cent quininic acid and about 2.6 per cent of a dark resinous substance. Of the base 36 per cent was unaltered, as was 90.9 per cent of the sensitizer.

On long standing in diffuse daylight and more rapidly in sunlight, 6,7-dimethoxy-1-benzyl-N-methyl-1,2,3,4-tetrahydroquinoline-1-carboxylic acid evolves carbon dioxide and changes to a yellow oil no longer soluble in alkali.[60] Benzylidene quinaldine, exposed to sunlight as a solid or in benzene solution, forms a dimer.[61]

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[52] Henri, V., and Angenot, P., *Compt. rend.*, **201**, 895 (1935), state that light of wavelengths greater than 2750A has no photochemical action on pyridine vapor. Ultraviolet light does not influence the nitration of pyridine in the vapor phase by nitrogen peroxide, Shoruigin, P. P., and Topchiev, A. V., *Ber.*, **69B**, 1874 (1936).

[53] Koller, G., *Ber.*, **60B**, 1920 (1927); *Chem. Abs.*, **22**, 80 (1928).

[54] Cantieni, R., *Helv. Chim Acta*, **17**, 1492 (1934); **18**, 3, 1420 (1935); *Chem Abs.*, **29**, 1034 (1935); **30**, 1662 (1936).

[55] Castiglioni, A., *Annali Chim. Appl.*, **27**, 256 (1937); *Brit. Chem. Abs.*, **A** (II), 478 (1937).

[56] de Carvalho, A. P., *Compt. rend.*, **200**, 60 (1935).

[57] John, H., and Behmel, G., *Ber.*, **66B**, 844 (1933); *Chem. Abs.*, **27**, 3713 (1933).

[58] For the behavior of *p*-methoxyquinoline, see Maschmann, E., *Ber.*, **59B**, 2825 (1926).

[59] John, H., and Andraschko, E., *Ber.*, **64B**, 1286 (1931); *Chem. Abs.*, **25**, 4275 (1931).

Scholl, Semp and Stix[62] find the arylpyrrolinoanthranolazyls to be nitrogenous, free organic radicals characterized by the absence of all tendency to dimerization, and resembling in stability toward air, acids and alkalies, the common dyes with normal valency. They are unstable toward light, being rapidly decolorized in solution by sunlight.

Histazarin dimethyl ether monoxime is converted by ultraviolet light into a mixture of the *trans* and *cis* forms.[63]

Visible light hastens the oxidation of N-methylphenazonium salts, producing mainly the 4-ketocompound, pyocyanine and phenazine, with small amounts of 2-hydroxyphenazine and 2-keto-N-methylphenazine. Photochemical oxidation of the ethosulfate yields 4-keto-N-ethylphenazine.[64]

ALKALOIDS

Lesure[65] found considerable ultraviolet absorption by solutions of caffeine, eserine salicylate, apomorphine hydrochloride, and quinine bisulfate. Solutions of eserine salicylate and apomorphine hydrochloride were only slightly discolored and no polarimetric change was observed after an exposure of 15 to 30 minutes. Solutions of cocaine hydrochloride or 1-per cent quinine bichloride or pilocarpine hydrochloride were not effected upon exposure for 30 minutes to the light of a Cooper-Hewitt lamp.

Nicotine. This alkaloid, its zinc chloride double salt, isomethiodide and dimethyliodide in water and in cyclohexane all exhibit a strong absorption band at 2650A.[66]

Ultraviolet light produces a change in nicotine solutions.[67] A 0.1-per cent solution when exposed in a quartz flask at 5 cm. from an ultraviolet source for 15 minutes showed a decided decrease in nicotine content. On the other hand, Custis claimed that a 40-per cent solution of commercial nicotine, when exposed for 30 minutes at 5 cm. from an iron arc showed an increase in the amount of nicotine present. Custis assumed that in this case some nicotine had been synthesized from certain oils present as impurities in the commercial sample. Attempts to synthesize nicotine photochemically have not been successful. Irradiating a 2-per cent aqueous solution of formaldehyde in 6.2*N* ammonia with which was admixed some copper carbonate gave, in experiments by Watson and Vaidya,[68] methylamine but no nicotine. This did not support the view of Bhargava and Dhar that nicotine is formed by the action of light on formaldehyde and ammonia.

The destruction of nicotine has, however, been repeatedly confirmed. In the presence of such sensitizers as potassium chromate, gold chloride, ferric nitrate, iodine and chlorophyll, sunlight causes decomposition of aqueous solutions of the alkaloid, present either as free base, salicylate, tartrate or malonate.[69] In tobacco, the rate of destruction was much less. Orange-red light was believed to be the most effective.

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[60] Hahn, G., and Stiehl, K., *Ber.*, **69B**, 2627 (1936); *Chem. Abs.*, **31**, 1815 (1939).

[61] Henze, M., *Ber.*, **70B**, 1273 (1937); *Chem. Abs.*, **31**, 5800 (1937).

[62] Scholl, R., Semp, H., and Stix, E., *Ber.*, **60B**, 1236 (1927); *Chem. Abs.*, **21**, 2684 (1927).

[63] Haq, M., Ray, J. N., and Tuffail-Malkana, M., *J. Chem. Soc.*, 1326 (**1934**).

[64] McIlwain, H., *J. Chem. Soc.*, 1704 (**1937**).

[65] Lesure, A., *J. pharm. Chim.*, **7**, 1,569; *Chem. Abs.*, **5**, 963 (1911).

[66] Lowry, T. M., and Lloyd, W. V., *J. Chem. Soc.*, 1376 (**1929**).

[67] Custis, H. H., *J. Frank. Inst.*, **184**, 878 (1917).

[68] Watson, H. E., and Vaidya, B. K., *J. Indian Chem. Soc.*, **11**, 441 (1934); *Brit. Chem. Abs.*, **A**, 1116 (1934).

[69] Plotnikow, J., and Weber, K., *Chem. Ztg.*, **55**, 237 (1931); *Chem. Abs.*, **25**, 2921 (1931).

It has been found that, after irradiation from a mercury arc, nicotine solutions have partially lost their effect on the blood pressure of dogs.[70] Wakeham and Tracy[71] found that although the reduction of toxicity might amount to 70 to 75 per cent in 75 minutes, it subsequently returns almost to the original value. Gant[72] observed that after 105 minutes of irradiation, a 0.1-per cent solution of nicotine had lost its basicity and that after 150 minutes it had acquired a slight acidity. At the neutral point the solution had a slight vasopressor activity. The product contained nicotinic acid, methylamine and unchanged nicotine. After 12 hours of irradiation the solution became neutral again, because of the destruction of the nicotinic acid, malonic acid and methylamine. Traces of nitrates, nitrites and ammonia were then found. The irradiation of nicotinic acid gave rise to the same end products. During the irradiation of nicotine, the solution darkened in color. This was ascribed to the formation of yellow oxidation products of nicotinic acid. The color is destroyed by further irradiation.

Quinine. The beautiful fluorescence induced in quinine solutions by visible and ultraviolet light has long been admired. Fabre[73] employed it in measuring the rate of elimination of quinine in the urine.[74] Similar fluorescence methods apply also to hydrastinine and other alkaloids.

The exposure of solutions of quinine salts to ultraviolet rays is said to have no effect on the paralyzing influence of these solutions on *Paramecium* and *Vorticella*,[75] notwithstanding the view of Roskin and Romanova[76] that irradiation increases the toxicity. Giordani[77] holds that, when exposed to ultraviolet rays in the presence of various substances, solutions of quinine undergo transformation into the toxic isomer, quinotoxin. Among the accelerators of the change are urethane and glycerol, which are frequently used in the preparation of solutions for intramuscular or intravenous injection. Alcohol, chloroform and hydrochloric acid were found ineffective in this change.[78] Macht and Teagarden[79] found that fluorescent solutions of quinine and quinidine sulfates became pharmacologically more active after ultraviolet irradiation.

Weigert[80] observed the absorption of oxygen during the irradiation of an aqueous solution of quinine sulfate in contact with air. The reaction velocity increased with increasing concentrations of the quinine sulfate, but was diminished by the addition of an acid. From experiments with gas mixtures containing variable proportions of oxygen, it was found that the reaction velocity increased continuously as the partial pressure of the oxygen diminished. With a mixture of nitrogen and oxygen containing only 0.6 per cent of oxygen, the velocity was about thirty times as large as with pure oxygen. The nature of the oxidation process appeared to vary with the proportion of oxygen.

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[70] Higgins, J. A., Ewing, P. L., and McGuigan, H. A., *J. Pharmacol.*, **42**, 213 (1931); *Chem. Abs.*, **25**, 5934 (1931).

[71] Wakeham, C., and Tracy, G. P., *J Am. Chem. Soc*, **55**, 1601 (1933); *J. Pharmacol.*, **44**, 295 (1932); *Chem. Abs.*, **26**, 3301 (1932)

[72] Gant, V. A., *J. Pharmacol.*, **49**, 408 (1933); *Brit. Chem. Abs.*, **1934A**, 196.

[73] Fabre, R., *Bull. soc. chim.*, **7**, 1024 (1925).

[74] See also Caujolle, F., *Bull. soc. chim. biol.*, **12**, 299 (1930).

[75] Milanesi, E., *Arch. farm sperim.*, **46**, 29, 33 (1928); Jirovec, O., and Bouse, V., *Z. Immunitätsf.*, **78**, 100 (1933); *Chem. Abs.*, **27**, 5114 (1933).

[76] Roskin, G., and Romanova, K., *Z. Immunitätsf.*, **62**, 147, 158; **63**, 452 (1929); *Chem. Abs.*, **24**, 5867 (1930).

[77] Giordani, K., *Annali chim. appl.*, **18**, 239 (1928); *Brit. Chem. Abs.*, **1928A**, 907.

[78] For the effect of ultraviolet on monoacyl derivatives of quinic acid, see Josephson, K., *Ber.*, **60B**, 2270 (1927).

[79] Macht, D. I., and Teagarden, E. J., Jr., *J. Pharmacol.*, **22**, 21 (1923).

[80] Weigert, F., *Festschrift W. Nernst*, **1912**, 464; *J. Chem. Soc.*, **102** (ii), 1120 (1912).

The reaction between quinine and chromic acid has been repeatedly investigated. The early observations of Goldberg [81] seemed to indicate that the velocity is dependent on the extent to which the radiations employed were absorbed by the chromic acid. Luther and Forbes [82] found, however, by using monochromatic radiations, that quinine is the substance which is light-sensitive, the chromic acid acting only as a filter. The total reaction velocity is proportional to the concentration of the hydrogen ion. The reaction appeared to occur in two stages: (1) the formation of "sensitized" quinine with a velocity proportional only to the light absorbed and (2) a reaction between this product and chromic acid with a velocity proportional to the concentration of the latter and of sulfuric acid.

Forbes and co-workers have conducted an elaborate series of investigations on the quantum yield at seven wave-lengths.[83] The quantum yields change with sulfuric acid concentrations at 4050, 3660, 3130 and 2800A and cannot be correlated with the effect of the acid on the extinction of either the quinine or the dichromate. Since the extinction coefficients are additive, it appears improbable that a stable complex is formed, analogous to that of uranyl oxalate. Instead, the reaction occurs in photochemically efficient clusters in the sense in which the term had been employed by Weigert. Irradiation of the dichromic acid did not increase its tendency to react wth non-activated quinine, except possibly at wave-lengths shorter than 2800A. The temperature coefficient of the reaction is 1.12. By graphical methods, the reaction order was found to be zero for quinine and 0.43 for dichromic acid or 0.86 for chromic acid. For sulfuric acid, it is only 0.07, indicating a subordinate role for this reactant. Ten quinine derivatives appear to give similar quantum yields. The values are of the order of 0.065 to 0.027 for quinine and most of the other alkaloids except cinchonine and cinchonidine, for which they are smaller. The low values are not due to the direct photolysis of the alkaloid. Probably a quantum is first absorbed by the quinoline group of the molecule for the logarithm of the quantum yield, at least in the case of quinine, is a linear function of the logarithm of the concentration of excited molecules. The activated molecules then reduce the chromic acid, one activated quinine molecule reacting with one of chromic (not dichromic) acid. In the case of all the alkaloids tested, the secondary hydroxyl group of the activated molecule appeared to be chiefly responsible for the reduction of the chromic acid. The significant suggestion is made that the energy absorbed by the quinoline group may be transferred to the secondary hydroxyl, this transfer occurring only when various photochemically inactive groups are substituted for hydrogen on the opposite side of the quinoline group. The energy transfer may be a resonance phenomenon.[83a] Quinine does not react at 4360A, where absorption is negligible, but decomposes at 4050A where absorption is considerable. With cinchonine, no photolysis occurs at 4050, but does occur at 3660A. With vuzin, the shift is toward the red; absorption is marked at 4360A. The quantum yield decreases as the number of quanta absorbed in the first centimeter of the reaction mixture increases. The yield is a maximum for quinine at 2800A and for cinchonine at 2540A.

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[81] Goldberg, E., *Z. wiss. Phot.*, **4**, 95 (1906); *J. Chem. Soc.*, **90** (ii), 514 (1906).

[82] Luther, R., and Forbes, G. S., *J. Am. Chem. Soc.*, **31**, 770 (1909).

[83] Forbes, G. S., Woodhouse, J. C., and Dean, R. S., *J. Am. Chem. Soc.*, **45**, 1891 (1923); Morton, D. S., *J. Phys. Chem.*, **33**, 1135 (1929); Forbes, G. S., Heidt, L. J., and Boissonas, C. G., *J. Am Chem. Soc.*, **54**, 960 (1932); Forbes, G. S., Heidt, L. J., and Brackett, F. P., Jr., *Ibid.*, **55**, 588 (1933), Forbes, G. S., and Heidt, L. J., *Ibid.*, **55**, 2407 (1933). Forbes, G. S., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 1 (1935); *Chem. Abs.*, **30**, 6648 (1936). Accurate absorption data for quinine at various acid concentrations were obtained in the course of this work.

[83a] Compare the views of Norrish on the simpler molecules of aldehydes.

Piperidine metavanadate turns black with liberation of piperidine upon irradiation with ultraviolet light.[84]

Light from a quartz mercury lamp causes a change in the absorption spectrum of ergometrine, which may serve to distinguish it from other ergot alkaloids.[85]

Strychnine in sulfuric acid is unaffected by the addition of small amounts of uranyl acetate; but on exposure to sunlight, the solution becomes violet, as a result of oxidation. This method may be used for the detection of 1×10^{-5} part of strychnine.[86] Under the same conditions of exposure, codeine and morphine give a deep blue color. None of the common alkaloids gives a similar reaction. This blue coloration may also be obtained by using a solution of uranyl acetate which alone has been exposed to the sunlight. This is due to the formation of formaldehyde, the addition of which to a solution of codeine in sulfuric acid with uranium or iron acetates in the absence of sunlight gives an intense blue coloration.

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[84] Baudisch, O., and Gates, F. L., *J. Am. Chem. Soc.*, **56**, 373 (1934).

[85] Bennekou, I., and Schou, S. A., *Dansk Tids. Farm*, **10**, 105 (1936); *Chem. Abs.*, **30**, 3944 (1936). See also Harmsma, A., *Pharm. Weekblad*, **65**, 1114 (1928); *Chem. Abs.*, **29**, 235 (1929).

[86] Aloy, J., Valdigué, A., and Aloy, R., *Bull. soc. chim.*, **39**, 792 (1926); *Chem. Abs.*, **20**, 2952 (1926).

Chapter 28

Effects of Light on Halogenation Reactions

Visible light of short wave-length and ultraviolet rays have long been emplo to assist in reactions involving halogenation. Chlorination of toluene in light make benzyl chloride, benzal chloride and benzotrichloride and, by hydrolysis the from, benzyl alcohol, benzaldehyde and benzoic acid, is a procedure of long sta ing. In fact, this application has received considerable commercial use.

During the World War I there was a shortage of amyl alcohol which stimula extensive investigations on the chlorination of butane, pentane and hexane to mo chlor compounds which in turn could be converted into the corresponding alcohols acetates.[1] Methods based upon these developments have been superseded in pract by entirely different processes, so that these photochemical reactions are at pres largely of historical or purely theoretical importance.

It is convenient to discuss halogenation reactions in a separate chapter si they depend for the most part upon the absorption of the light energy by halogens rather than by the organic reactants. In this discussion, the orga compounds are considered in about the order in which their photochemical re tions have been considered in previous chapters. Due consideration must be gi to the possibility that in some instances, particularly those in which unsatura organic compounds play a part, there may be an absorption of light by the orga substance in addition to that absorbed by the halogen.

Schumacher[2] has reviewed the photochemical reactions of the halogens w aliphatic compounds. Hass, McBee and Weber[3] conducted photochemical chl nations of propane, *n*- and iso-butane and *n*- and iso-pentane at temperatures from −60° to 300° and studied the reaction in the dark at temperatures up 600°C. They separated the products by distillation and identified them rigorou When pyrolysis temperatures were avoided, no rearrangements of the carbon sk ton occurred during either the photochemical or the thermal chlorinations. Ev possible monochloride derivable without such rearrangement was found to always formed. This generalization extended to all polychlorides studied. Phc chlorination of liquid 1-chloro-3-methyl-propane at 7°C. yields 7 or 14 per c of overchlorinated product when a given amount of chlorine is added slowly rapidly.[4]

Although Tolloczko[5] obtained by the irradiation of streaming mixtures chlorine and natural gas at 80 to 100°C. by an ultraviolet lamp, such products methyl chloride, dichlormethane, carbon tetrachloride and di-, tetra- and he chlorethane, Baskerville and Riederer[6] found it was the blue rather than ultraviolet rays which accelerate the reactions. Brooks, Smith and Essex[7] found similarly that once the chlorination of pentane had been started, it would proceed very smoothly in diffused daylight. Mott and Bedford[8] demonstrated that the flaming carbon arc gave more rapid chlorination of isoamyl chloride, isopentane or benzene than did the quartz mercury arc. Furthermore, little efficiency was lost by the use of glass containers when the flaming arc was used.

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[1] de Lattre, J., French P. 468,244, Feb. 9, 1914; *J. Soc. Chem. Ind.*, **33**, 953 (1914).

[2] Schumacher, H. J., *Angew. Chem.*, **49**, 613 (1936).

[3] Hass, H. B., McBee, E. T., and Weber, P., *Ind. Eng. Chem.*, **27**, 1190 (1935); **28**, 333 (19

[4] Hass, H. B., McBee, E. T., and Hatch, L. F., *Ind. Eng. Chem.*, **29**, 1335 (1937).

[5] Tolloczko, S., *Abhandl. Krakauer Akad. Wissensch.*, **52**, 307; *Chem. Zentr.*, **84**, II, 99 (19 *Chem. Abs.*, **8**, 1282 (1914).

[6] Baskerville, C., and Riederer, H. S., *Ind. Eng. Chem.*, **5**, 5 (1913).

In subsequent experiments on the chlorination of methane, Bedford[9] found diffused daylight to produce little or no reaction as long as the percentage of chlorine in the gases was low. Upon suddenly exposing such mixtures to the white flame arc there was an instantaneous explosion of the gases.

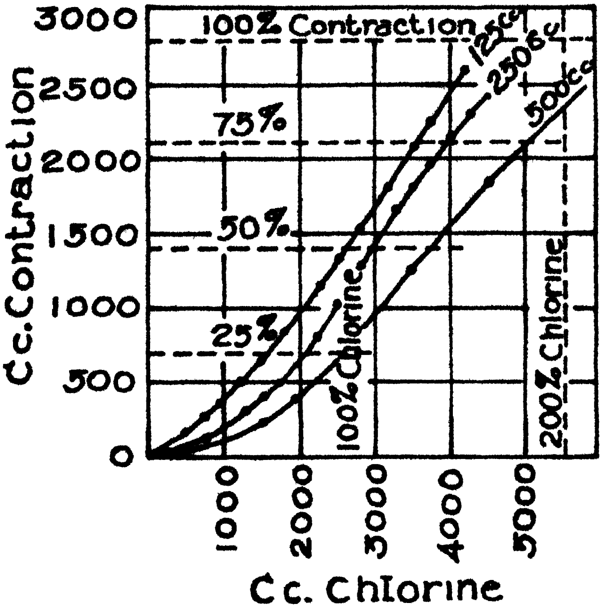

FIGURE 116. Chlorination of Natural Gas.

Figure 116 shows the results reported on the chlorination of natural gas at room temperature in the presence of various quantities of chlorine. After each exposure the gases were cooled by shaking up with water which removed the hydrogen chloride and condensed such reaction products as were liquid at the temperature of the water. The volume of the residual gases was then noted and the contraction from the original gas volume calculated. Starting with three liters of natural gas there was always an unreacting residue of about 200 cc. showing that about 2800 cc. would react with chlorine.*

To avoid the formation of carbon tetrachloride, Bedford tried filling the reaction chamber with cracked ice. He reasoned that in this manner he should obtain only the di- and tri-substitution products, since methyl chloride is a gas at the temperature of ce and the other products might be expected to condense out before forming the tetrachloride. The first experiment, however, indicated the difficulty of securing proper gas circulation. After many variations in the set-up, Bedford employed the apparatus shown in Figure 117. An 8-liter, two-necked Woulfe flask, with the bottom removed, was placed over a single ice cake chipped to nearly fill the flask. As the ice melted in the top of the reaction chamber, the flask settled upon it, keeping the ice in the top of the chamber where the cooling is most needed, until the bottom of the flask touched the bottom of the vat. The dotted lines show the point of highest temperature as shown by the melting of the ice. Upon starting the reaction, by means of the white flame arc, with the chlorine content of the gases about one in eight, the circulation was found to be rapid and violent. It was found that 2.6 cubic feet of natural gas gave 166 cc. of reaction products. This is equivalent to about seventeen gallons per thousand cubic feet. This included methylene chloride and chloroform dissolved in the water, which were separated by distillation.

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[7] Brooks, B. T., Smith, D. F., and Essex, H., *Ind. Eng. Chem.*, 10, 511 (1918).

[8] Mott, W. R., and Bedford, C. W., *Ind. Eng. Chem.*, 8, 1029 (1916).

[9] Bedford, C. W., *Ind. Eng. Chem.*, 8, 1090 (1916).

* The horizontal dotted lines in Figure 116 represent percentages of the total contraction obtained and aid in the study of the curves.

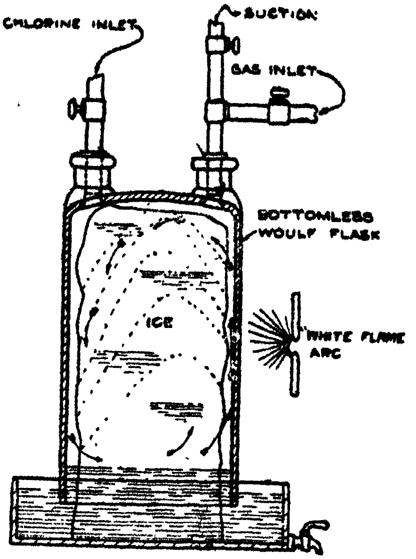

FIGURE 117. Bedford's Apparatus for Chlorination of Methane.

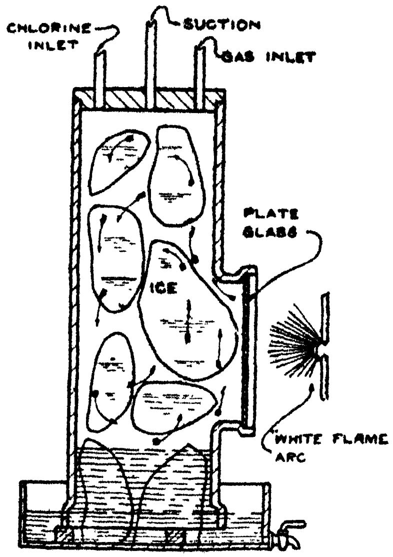

FIGURE 118. Modification of Bedford's Apparatus.

A large wooden reaction chamber, practically duplicating Figure 118, 28" by 28" by 44", inside dimensions, was built for carrying out the reaction on a large scale. In one experiment using 250 cubic ft. of natural gas, the rate of consumption varied from 14 to 30 cubic feet per hour and several gallons of product resulted. The analysis of the liquid reaction product separating out under the water was as follows, the percentages being by volume:

Table 21.—Chlorides from Natural Gas.

Methylene Chloride	Chloroform	Carbon Tetrachloride	Ethane Chlorides
35	35	5	20

The analysis of the part soluble in the water and separated by distillation was:

60	28	1.5	6

About 14 per cent of the reaction product dissolves in the water produced from the melting of the ice by the heat of the reaction. This soluble portion may be entirely recovered by distilling off 5 to 10 per cent of the water, the methyl chloride coming over with the distillate, and the residue being about a 5-per cent solution of hydrochloric acid, provided that no water has been added except that produced by the melting of the ice.

About 135 pounds of ice were necessary for the production of one gallon of product having the composition given above.

According to Padovani and Magaldi,[10] the condition necessary for obtaining a maximum yield of monochloromethane in the photochemical chlorination of methane by use of the mercury arc is to have the ratio of methane to chlorine between 15 to 1 and 19 to 1. Then up to 29 per cent of chlorine goes to methyl chloride and 80 per cent of the total chlorine is utilized. The ratio of methyl chloride to chlorine present in liquid products is 1.75. The efficiency of energy utilization is extremely low. This is the most serious obstacle to the commercial utilization of the process.

Comparatively few theoretical studies have been made of these chlorination reactions. In the case of methane, the chlorination is a chain process, quantum yields of 10^4 being found.[11] The reaction is strongly inhibited by traces of oxygen.

From an analogy between this reaction and the hydrogen-chlorine combination, Jones and Bates[12] suggest that it occurs by virtue of chlorine atoms and free methyl radicals, the latter formed by the action of the chlorine atom on methane. From their rate experiments, conducted with a flowing system in a glass spiral illuminated by a Pyrex mercury arc, they were unable to determine whether the methyl group or a hydrogen atom carried the chains. Simple considerations of the collision mechanism of a chlorine atom with the methane molecule made the former seem the more probable.

The total chlorination of pentane in the liquid phase and with rigid exclusion of oxygen which is an inhibitor was studied by Stewart and Weidenbaum.[13] Using light of 3650A, they found a quantum efficiency of 192. The reaction rate is proportional to the chlorine concentration at constant light intensity. The mechanism involves the reactions:

$$
\begin{aligned}
Cl_2 + h\nu &\longrightarrow Cl + Cl. \\
Cl + C_5H_{12} &\longrightarrow HCl + C_5H_{11} \\
C_5H_{11} + Cl_2 &\longrightarrow C_5H_{11}Cl + Cl.
\end{aligned}
$$

This mechanism fulfills the necessary conditions that the overall reaction, as well as every step, be exothermic or have but a small energy of activation. The correct experimental rate law is derivable if the chain-terminating step is taken to be a formation of chlorine molecules at the wall or inert molecules.

Benrath and Hertel[14] found that perfectly purified and dried carbon tetrachloride contains free chlorine after several days of exposure to light. The amount of decomposition is not sufficiently great to hinder the use of carbon tetrachloride as a solvent in which to study the photochlorination of various aliphatic compounds. Since halogen compounds are frequently used as solvents, it may be noted that chloroform is comparatively unstable under the influence of ultraviolet radiation[15] and further that trichloroethylene is on occasions a somewhat fickle solvent disengaging hydrogen chloride.[16]

During the period from 1912 to about 1925 a considerable number of patents dealing with the chlorination of various saturated hydrocarbons were issued. It is feasible here to do no more than cite these, since most deal with details of apparatus for applying ultraviolet rays.[17]

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[10] Padovani, C., and Magaldi, F., *Giorn. Chim. Ind. Applicata*, **15**, 1 (1933); *Chem. Abs.*, **27**, 3443 (1933).

[11] Coehn, A., and Cordes, H., *Z. physik. Chem.*, **9B**, 1 (1930).

[12] Jones, L. T., and Bates, J. R., *J. Am. Chem. Soc.*, **56**, 2282 (1934)

[13] Stewart, T. D., and Weidenbaum, B., *J. Am. Chem. Soc.*, **57**, 1702 (1935)

[14] Benrath, A., and Hertel, E., *Z. wiss. Phot.*, **23**, 30 (1924).

[15] Kailan, A., *Monatsh.*, **38**, 537 (1917); *J. Chem. Soc.*, **112**, i, 209 (1917).

[16] Elsner, W., *Chem. Z.*, **41**, 901 (1917).

Graul and Hanschke[18] boiled normal hexane in an enameled vessel on a water-bath, and passed the vapors through a vertical fractionating column into a second vessel in which they were mixed with chlorine. The mixture, containing an excess of hexane vapor, passed into a third vessel in the middle of which a mercury lamp was burning. The vapors leaving this reaction vessel were passed through a condenser in which the chlorhexane and the excess of hexane condensed and passed through a siphon into a distillation vessel, while the hydrochloric acid formed during the process was allowed to escape from the circuit. The fractionating column attached to the first vessel was maintained at a temperature that allowed only hexane to pass, while chlorhexane remained in the still and increased in quantity. To prepare monochlor-isoheptane, a Galician petro-

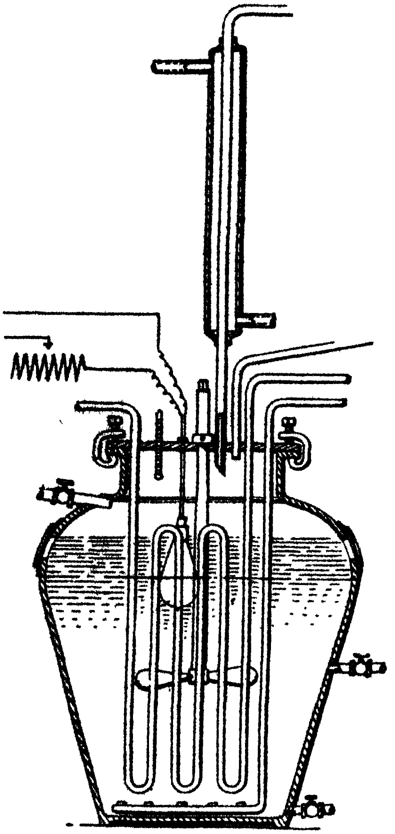

FIGURE 119.

Apparatus of Brooks, Essex and Smith for Chlorinating Liquid Hydrocarbons.

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[17] Blanc, C., U. S. P. 1,248,065, Nov. 27, 1917; Rodebush, W. H., U. S. P. 1,402,318, Jan. 3, 1922; Okinaka, T., and Sakai, S., Japanese P. 35,994; *Chem. Abs.*, 15, 1535 (1921); Japanese P. 39,940, July 16, 1921; *Chem. Abs.*, 16, 3560 (1922); DuPont Co., French P. 453,406, June 21, 1913; Pfeiffer, I., and Szarvasy, E., U. S. P. 1,012,149, Dec. 19, 1911; *J. Soc. Chem. Ind.*, 32, 91 (1912); Snelling, W. O., U. S. P. 1,523,563, Jan. 20, 1925; 1,285,823 and 1,325,214; *Chem. Abs.*, 14, 369 (1920); U. S. P. 1,271,790, July 9, 1918; 1,523,563, Jan. 20, 1925; Keyes, F. G., U. S. P. 1,237,652, Aug. 21, 1917; Sparre, F., and Masland, W. E., U. S. P. 1,379,367, May 24, 1921; Tompkins, H. K., British P. 780, Jan. 18, 1915; *J. Soc. Chem. Ind.*, 34, 1225 (1915); Leiser, R., and Ziffer, F., U. S. P. 1,459,777, June 26, 1923; Söll, J., and Runkel, K., German P. 491,316, Dec. 12, 1922; Keyes, F. G., U. S. P. 1,198,356, *Chem. Abs.*, 10, 2315 (1916); Lacey, B. S., U. S. P. 1,308,760; *Chem. Abs.*, 13, 2219 (1919).

[18] Graul, O., and Hanschke, G., U. S. P. 1,032,822, July 16, 1912.

leum fraction consisting chiefly of isoheptane was placed in a lead-lined vessel provided with fractionating column and raised to the boiling point, at a pressure of 50 mm. of mercury. The vapors were mixed with chlorine and passed through a vessel containing a mercury lamp. In order to chlorinate 10 parts of hydrocarbon, about 7 parts of chlorine were necessary. The chlorination product consisted chiefly of a mono-chlorisoheptane which boils at about 140°C. and contains 26.5 per cent of chlorine. By treating, in a similar manner, the repeatedly purified fraction of Galician petroleum which boils at from 75° to 81°C., a product was obtained boiling between 135° and 145°C., and containing 29.1 per cent of chlorine, whereas pure monochlorhexamethylene contains theoretically 29.8 per cent of chlorine.

A few patents dealt with the chlorination of liquid hydrocarbons. Brooks, Essex and Smith[19] emphasized the necessity of introducing the chlorine in minute bubbles at a point in the liquid remote from that at which the rays of light enter, and agitating so as to maintain a large excess of hydrocarbon in the zone where the reactions occur. It was believed that this led to the production chiefly of monochlor- products (butyl, pentyl and hexyl chlorides) from gasoline, useful in the manufacture of artificial "amyl acetate." (See Fig. 119.) The unchanged oil is separated from the chlorides by fractional distillation. If dichlorides are to be produced, the container is charged with monochlorides rather than with hydrocarbons. Even solid materials as paraffins may be used if they are melted or dissolved in carbon tetrachloride.

Brooks and Padgett[20] chlorinated solar oil in this manner and subjected the dichloride obtained to a high temperature in the presence of a catalyst. This treatment split off hydrochloric acid and produced unsaturated hydrocarbons with an iodine number of from 120 to 150 suitable for the formation of "drying" films like those of linseed oil.[21]

After a lapse of nearly ten years, patents in this field have again begun to appear. In a continuous flow method for the vapor phase photochlorination of the saturated aliphatic hydrocarbons with three to five carbon atoms, as butane or isobutane, Britton, Coleman and Hadler[22] employ surfaces in contact with the reacting mixture cooled to a temperature (below 250°) which prevents the formation of chloroölefines. For preparing monochloro- derivatives, Teichmann, Klein and Rathemacher[23] treat a paraffin hydrocarbon material, such as a pentane fraction, in the liquid phase while exposed to ultraviolet light with a reagent consisting of polychloro- derivatives of the hydrocarbons. The reaction products are then submitted to a reaction with chlorine under such pressure as to maintain the reaction products in the liquid phase, so that monochloro- and polychloro- compounds and hydrogen chloride are formed. The hydrogen chloride is removed and the chlorocompounds separated into two fractions, one containing the mono- and the other the polychloro- derivatives.

According to Sharp,[24] a material containing a high percentage of propane and a compound such as the lower chloropropanes convertible into a trichloropropane are treated with chlorine in the presence of a chlorination catalyst such as copper chloride or ferric chloride under the influence of actinic rays, and in a plurality of stages at increasing temperatures.

In their studies of the higher polychlorides obtainable by the chlorination of 2-chloro-2-methylpropane in the liquid phase, Rogers and Nelson[25] used ordinary incandescent lamps for activation. They were chiefly concerned with the characterization of the various higher chlorides obtainable by fractional distillation. There were obtained from 3500 cc., 305 cc. of $(CH_3)_2CClCH_2Cl$, 600 cc. of $(CH_3)_2CClCHCl_2$, 875 cc. of $(CH_3)_2CCl(CH_2Cl)_2$, 460 cc. of 1,1,2,3-tetrachloro-2-methylpropane and 130 cc. of $ClC(CH_2Cl)_3$. Chlorination of 400 cc. of the first fraction of these gave 140 gm. of $(CH_3)_2CClCCl_3$. Chlorination of the $CH_3CH(CH_2Cl)_2$ gave the 1,2,3,-trichloro- and 1,1,2,3-tetrachloro- derivatives. $(CH_3)_2CClCH_2Cl$ gave the 1,1,2- and the 1,2,3-trichloro- derivatives. In general, the presence of a chlorine atom on a carbon atom promoted further substitution on that atom.[26]

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[19] Brooks, B. T., Essex, H., and Smith, D. F., U. S. P. 1,191,916, July 18, 1916.

[20] Brooks, B. T., and Padgett, F. W., U. S. P. 1,220,821, March 27, 1917.

[21] Details of another chlorination process involving both liquid and vapor phase chlorination successively have been given by Boyd, H. T., U. S. P. 1,293,012, Feb. 4, 1919.

[22] Britton, E. C., Coleman, C. H., and Hadler, B. C., U. S. P. 1,954,438, April 10, 1934, to Dow Chemical Co.; *Chem. Abs.*, **28**, 3739 (1934).

[23] Teichmann, C. F., Klein, H., and Rathemacher, C. P., U. S. P. 2,015,044, Sept. 17, 1935; *Chem. Abs.*, **29**, 7338 (1935).

[24] Sharp, W. F., U. S. P. 2,001,039, Aug. 6, 1935; *Chem. Abs.*, **29**, 6252 (1935).

[25] Rogers, A. O., and Nelson, R. E., *J. Am. Chem. Soc.*, **58**, 1027 (1936).

Chlorination of Chloroform. Gault and Truffault[27] found chlorine without action on chloroform in the dark or when exposed to radiations of wave-length longer than about 6390A. Violet light had a slight effect and ultraviolet rays (3000 to 3400A) a great one. The reaction begins at −5°C. and becomes rapid at 5-10°C. Dry chlorides of calcium, zinc or aluminum act to some degree as catalysts, but ferric chloride appeared to inhibit the reaction entirely by acting as an internal filter. Even in the absence of any stimulus other than ultraviolet, the reaction is complete and carbon tetrachloride results. Benrath and Hertel[28] observed an induction period of about thirty minutes when the reaction was carried out in carbon tetrachloride.

In the vapor state, the rate of the reaction at 50 to 70°C. is proportional to the square root of the chlorine concentration and to the square root of the absorbed energy.[29] The temperature coefficient is 1.45 between 50 and 60°C. Oxygen practically suppresses the formation of carbon tetrachloride and yields phosgene. The reaction has a chain mechanism, with the following four reactions:

$$\begin{aligned}
&Cl_2 + h\nu \longrightarrow Cl + Cl. \\
&Cl + CHCl_3 \longrightarrow CCl_3 + HCl \\
&CCl_3 + Cl_2 \longrightarrow CCl_4 + Cl \\
&CCl_3 + CCl_3 \longrightarrow Cl_2 + 2CCl_4.
\end{aligned}$$

Chapman[30] finds the average quantum yield of hydrogen chloride 1.70 in the chlorine-sensitized photoöxidation of chloroform in carbon tetrachloride solution; in the vapor phase it is about 100.

In the replacement of bromine by chlorine in bromotrichloromethane, Noddack[31] reported a quantum yield of unity at high concentrations. This was decreased to about 0.2 when dilute solutions were used. A later study by Grüss[32] indicated a value of 0.88, independent of the concentration. These workers assumed that the reaction is a simple replacement, and determined the rate of the change by measuring the absorption changes which attended the liberation of the bromine. The possibility that an error might arise because of the formation of a bromochloride led Vesper and Rollefson[33] to examine the reaction again. They found the reaction more complicated than had been assumed, a chain process being involved. They employed the group of lines at 3660A isolated from the mercury arc radiations by means of a filter, in order to avoid the decomposition of bromotrichloromethane which Paterno[34] had found to occur in the region below 3350A. By spectrographic methods and a knowledge of the original chlorine concentration, it was possible to calculate the concentrations of chlorine, bromine and bromine chloride present at any time. The reaction was found to be

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[26] For the chlorination of methyl chloride and dichloromethane, see Dachlauer, K., and Schmitzler, E., French P. 816,990, Aug. 21, 1937, to I. G. Farbenind. A.-G.; *Chem. Abs.*, **32**, 2142 (1938); German P. 657,978, May 25, 1938; *Chem. Abs.*, **32**, 5856 (1938).

[27] Gault, H., and Truffault, R., *Compt. rend.*, **179**, 467 (1924); *Chem. Abs.*, **19**, 35 (1925).

[28] Benrath, A., and Hertel, E., *Z. wiss. Phot.*, **23**, 30 (1924).

[29] Schumacher, H. J., and Wolff, K., *Z. physik. Chem.*, **25**, 161 (1934). See, however, Schwab, G. M., and Heyde, V., *Z. physik. Chem.*, **B8**, 147 (1930).

[30] Chapman, A. T., *J. Am. Chem. Soc.*, **56**, 818 (1934).

[31] Noddack, W., *Z. Elektrochem.*, **27**, 359 (1921).

[32] Grüss, H., *Z. Elektrochem.*, **29**, 144 (1923).

[33] Vesper, H. G., and Rollefson, G. K., *J. Am. Chem. Soc.*, **56**, 1455 (1934).

$$Cl_2 + CBrCl_3 \longrightarrow BrCl + CCl_4$$

no hexachloroethane being formed. (A second reaction in which free bromine and two molecules of carbon tetrachloride are formed occurred to only a negligible extent.) The rate of the reaction varied directly with the chlorine concentration raised to a power between 1. and 1.5, and with the bromotrichloromethane concentration to a power somewhat greater than 0.5. The rate was markedly retarded by bromine chloride. It was not affected by the total pressure, but was doubled by increasing the temperature from 28 to 50°C. No dark reaction occurred. The incident light intensity enters the rate law by a power slightly greater than 0.5. Inert gases had practically no effect on the reaction rate. The quantum yield was found to be much higher than previous workers had indicated. It reached at least thirty at the beginning of the reaction but decreased to less than ten when the concentration of the bromine chloride had become large. The quantum yield could be decreased by lowering the concentrations of either of the two reactants.

A little attention has been devoted to iodination reactions of the saturated simple paraffins. Iodine derivatives of the paraffin series, excepting liquid methane, may be obtained by mixing the hydrocarbon in the dark with hydriodic acid and subjecting the mixture to the action of light rays of short wave-length or to the silent electric discharge. The reaction temperature may be reduced, according to the Badische Co.[35] by operating under diminished pressure.

The photochemical formation of phosgene in the action of chlorine on chloroform in the presence of oxygen is inhibited by such substances as methanol, ethanol and ammonia. The duration of the inhibition is proportional to the quantity of the inhibitor.[36] It is due to the removal of the chlorine atoms by the inhibitor, since, if the latter is first chlorinated, it ceases to affect the reaction.

UNSATURATED HYDROCARBONS

A few early patents were devoted to the chlorination of unsaturated hydrocarbons. Eldred and Mersereau[37] state that olefins produced by cracking oil may be treated with chlorine in the presence of rays of a mercury-vapor lamp in order to obtain chlorinated products. They noted that the operation requires caution since the reaction is violent. Ragaz, Paillard and Briner[38] passed 30 cc. of kerosene over iron turnings in an iron tube at temperatures of 550 to 800°C. and obtained about 13 liters of gas containing about 30 per cent of unsaturated compounds. By passing a slight excess of chlorine into the gas as it was formed in diffused daylight about 57 per cent of the gas was converted into a mixture of chlorinated hydrocarbons. This gave fractions distilling at 65-100°C., 70.69 per cent chlorine; 100-125°C., 73.41 per cent; 125-150°C., 75.14 per cent. These were mobile fluids whose flash points were 5°C., 19°C. and 36°C., respectively.

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[34] Paterno, E., *Jahresb. Chem.*, **24**, 259 (1871).

[35] Badische Anilin u-Soda Fabrik, German P. 266,119, Oct 31, 1911.

[36] Schumacher, H. J., and Sundhoff, D., *Z. Elektrochem*, **21**, 499 (1935).

[37] Eldred, B. E., and Mersereau, G., U. S. P. 1,234,886, July 21, 1917.

[38] Ragaz, Y., Paillard, H., and Briner, E., *Helv. Chim. Acta*, **8**, 225 (1925); *J. Soc. Chem. Ind.*, 1925B, 580.

They readily dissolved sulfur, iodine or white wax. The use of ultraviolet light or the addition of catalysts did not improve the yield of non-flammable solvents.

In a patent of the I. G. Farbenindustrie[39] 1,1,2-trichloroethane is obtained by direct addition of vinyl chloride and chlorine gases without the use of a solvent by the aid of light or heat.

The rate of addition of chlorine to ethylene is accelerated by the rays of the mercury arc.[40] Trichlorohydrin is obtained by further chlorination, in the presence of a sulfur compound such as sulfur dioxide, sulfur chloride, sulfuryl chloride, of propylene chloride or a similar compound obtained by saturating unsaturated hydrocarbons with chlorine.[41] The sulfur compound should not exceed 1 per cent of the amount of chlorine. Sulfur dioxide and chlorine may either be introduced separately or mixed. The reaction is effected in direct sunlight or ultraviolet rays or the light of the flaming arc. The product is separated from any unchanged propylene chloride by distillation.

In the chlorination of propylene dichloride with metallic iron present, ultraviolet light and low temperatures favor the production of $CHCl(CH_2Cl)_2$. Higher temperatures without irradiation favor the formation of $CHCH_3Cl.CHCl_2$.[42]

Stewart and Weidenbaum[43] investigated the reaction between chlorine and ethylene, using light from a 500-watt tungsten lamp and filters. At 4360A the quantum yield appeared to be large. During the early part of the reaction there appeared to be a logarithmic relation between the chlorine pressure and the time, as well as a linear relation between the reaction rate and the light intensity. The experimental results could be expressed by mechanisms involving either atomic chlorine or Cl_3; the collision efficiency of ethylene with either should be high, since the reaction rate is independent of the ethylene concentration over wide limits The rate was thought to be determined by the rate of liberation of atomic chlorine from an intermediate, $C_2H_4Cl_3$. Any hydrogen added to the reaction vessel appeared not to react until the ethylene-chlorine reaction had gone to completion. When the reaction was carried out in solution in ethylene dichloride, it was very rapid and less than 10 per cent of the chlorine was involved in substitution reactions. But with pentane as the solvent, from 37 to 73 per cent of the chlorine entered into substitution and this could be increased by increasing the ethylene-to-chlorine ratio.

Dickinson and Leermakers[44] found it possible to chlorinate tetrachloroethylene in carbon tetrachloride solution by the action of blue light in the absence of oxygen. The chlorination proceeds as a chain reaction with a large quantum yield (300-2500) and at a rate proportional to the square root of the intensity of illumination. In the presence of oxygen, in place of a simple inhibition, there occurs a chlorine-sensitized oxidation to trichloroacetyl chloride and phosgene.[45] This reaction proceeds in solution with a comparatively small quantum yield (1 to 2.5) and at a rate proportional to the light intensity, and to the chlorine concentration.[46] The work on the chlorination of tetrachloroethylene has been extended to the gas phase by Dickinson and Carrico,[47] who conducted it at temperatures below 40°C. and followed the rate by measuring in an ingenious apparatus the change in pressure. In the absence of oxygen, the chlorination proceeded with the formation on the walls of the vessel of colorless crystals having the odor of hexachloroethane. In the presence of oxygen little if any chlorination occurred, but phosgene and trichloroacetyl chloride were obtained. The rate of the chlorination was proportional to the chlorine concentration and to the square root of the intensity of the light absorbed.

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[39] British P. 298,084, Sept. 30, 1927, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.*, **B**, 122 (1929)

[40] Kinumaki, S., *J. Chem. Soc. Japan*, **54**, 142 (1933); *Chem. Abs.*, **27**, 2369 (1933).

[41] British P. 168,676, Feb. 18, 1921, to Glysyn Corporation; *Chem. Abs.*, **17**, 771 (1923).

[42] Levine, A. A., and Cass, O. W., British P. 471,188, Feb. 28, 1936, to E. I. DuPont de Nemours and Co.; *Brit. Chem. Abs.*, **B**, 1309 (1937).

[43] Stewart, T. D., and Weidenbaum, B., *J. Am. Chem. Soc.*, **57**, 2036 (1935).

[44] Dickinson, R. G., and Leermakers, J. A., *J. Am. Chem. Soc.*, **54**, 3852 (1932).

[45] Cf. Besson, A., *Compt. rend.*, **121**, 125 (1895).

[46] See also Dickinson, R. G., and Leermakers, J. A., *J. Am. Chem. Soc.*, **54**, 4648 (1932).

In the chlorine-sensitized photo-oxidation in the gas phase about 300 molecules of tetrachloroethylene were oxidized for each quantum (3358A) absorbed. There was no strong dependence of the yield on the concentrations or light intensity.

The chlorination of *trans*-dichloroethylene at 80-95°C. by the 4358A line of the mercury arc is a chain reaction.[48] For a chlorine pressure of 100 mm. and an absorption of 10^{16} quanta per minute, the quantum yield is 7×10^3 and the temperature coefficient 1.13. For pressures of the dichloride greater than 20 mm., the rate is given by

$$\frac{d(C_2H_2Cl_4)}{dt} = k(I_{abs})^{\frac{1}{2}}(Cl_2)$$

The mechanism involves the reactions:

$$\begin{aligned} Cl + C_2H_2Cl_2 &\longrightarrow C_2H_2Cl_3 \\ C_2H_2Cl_3 + Cl_2 &\longrightarrow C_2H_2Cl_4 + Cl \\ 2C_2H_2Cl_3 &\longrightarrow 2C_2H_2Cl_2 + Cl_2 \end{aligned}$$

The reaction is strongly inhibited by the presence of oxygen.

The reaction with the *cis*- compound is very similar.[49] In this case, a sensitized oxidation with greater quantum yield does not occur. In the chlorination of trichloroethylene, the rate of formation of pentachlorethane is proportional to the chlorine concentration and the square root of the energy absorbed. Only at pressures below 5 mm. is it dependent on the concentration of trichloroethylene. The temperature coefficient is 1.20. The quantum yield (chlorine at 100 mm. and 1.7×10^{14} quanta per second) is 700. The reaction is inhibited by oxygen and a sensitized oxidation occurs.

Notwithstanding the many instances of inhibition of chlorination processes by oxygen, Willard and Daniels[50] find the rate of photobromination of liquid tetrachloroethylene with light of 4360A to be increased by small amounts of oxygen. But when one atmosphere of oxygen is used, the photobromination is almost completely inhibited, probably because of a bromine-sensitized oxidation. The bromination products inhibit the reaction but the concentration of tetrachloroethylene is not important. The quantum yield varies enormously from 24 to only 0.009 (moles of bromine disappearing per quantum) with values of 1 to 5 the most frequent. The free radical C_2Cl_4Br is believed to play a part in the reaction mechanism and it is suggested that the life period of this radical is much shorter at higher temperatures and that it is stabilized by oxygen.

These authors also found that the photobromination of chloroform does not occur at 2650A in the absence of oxygen, although a reaction takes place in the presence of small amounts of the latter. Kaufmann and Hansen-Schmidt[51] found *α,β*-diiodoethylene to react rapidly with bromine in carbon tetrachloride in light, but not in darkness.

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[47] Dickinson, R. G., and Carrico, J. L., *J. Am. Chem. Soc.*, **56**, 1473 (1934); see also Stewart, T. D., and Smith, D. M., *Ibid.*, **51**, 3082 (1929).

[48] Müller, K. L., and Schumacher, H. J., *Z. physik. Chem*, **B35**, 285 (1937)

[49] Müller, K. L., and Schumacher, H. J., *Z. physik, Chem*, **B35**, 455 (1937); *Z. Elektrochem*, **43**, 807 (1937)

[50] Willard, J., and Daniels, F., *J. Am Chem. Soc.*, **57**, 2240 (1935).

Schultze[52] briefly called attention to the possibility of a bromine-sensitization of the oxidation of unsaturated hydrocarbons.

The Action of Iodine on Unsaturated Hydrocarbons. Badger and Urmston[53] suggested the possibility of separating two types of iodine molecule, only one of which absorbs the 5461A line, by causing the activated type to react photochemically with hexene vapor.

The photosensitizing action of iodine upon the decomposition of ethylene iodide in carbon tetrachloride solution has been studied by Schumacher and Wiig.[54] The rate is proportional to the concentration of the ethylene iodide and to the square root of the absorbed light energy. At 100°C. the temperature coefficient is 1.57 per 10°. The mechanism involves a chain of simple type carried by iodine atoms. Murthi[55] finds their data consistent with every collision between iodine atoms in solution resulting in the formation of iodine molecules. According to Schumacher and Stieger[56] the quantum yield decreases markedly in the band region at 5461 or 5770A as compared with that at 4360A. Their results indicate that at 5460A and 5780A, excited iodine molecules for the most part give up their energy without dissociating. Murthi[57] calculates from their data and the assumption that every collision between iodine atoms produces a molecule, that the energy of activation is 12 kcals. as compared with an observed value of 11.8. No steric factor is needed to bring the calculated and observed rates into agreement. Dickinson and Nies,[58] objected that Schumacher's conclusion that excited molecules in the band region largely lose their energy without dissociating was the result of a failure to take into account possible variations in the absorption of the green and blue lines. They repeated rate measurements at various wave-lengths giving special consideration to the distribution of energy. As a result, they concluded that the rates are only slightly lower in the region of discontinuous absorption than in that of continuous absorption. The rate of the reaction depends only upon the rate of production of iodine atoms, irrespective of whether they are formed by primary dissociation or as a result of collisions of excited molecules, presumably with solvent molecules.

When an equimolar quantity of iodine was added to 0.01 molar solutions of 1-butene in methylene chloride or chloroform and the solutions illuminated, 90 per cent of the iodine disappeared in three hours in the former solvent at −60 to −90°C. and 98 per cent in the latter at −60 to −70°C.[59] On irradiating the solutions in quartz by a spark between high-tungsten steel electrodes, the iodine was evolved quantitatively within an hour in three stages. At 20°C. for 100 hours, 84 per cent of the iodine was evolved, also in stages.

In the quantitative photoiodination (4360, 5460, 6440A) of the first six simple olefins at −55°C., the quantum yields vary as much as forty-fold. They fall off with decreasing frequency of light to the order of 0.01 at 6440A.[60] The rate is nearly proportional to the concentrations of olefins and of iodine, and to the light intensity. 1,2-Diiodobutane, prepared at low temperatures, was photolyzed at −60, −20 and 25°C., the quantum yields increasing from 0.7 to 1.15.

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[51] Kaufmann, H. P., and Hansen-Schmidt, E., *Arch Pharm.*, **263**, 32 (1925); *J. Chem. Soc*, **128**, *A(II)*, 554.

[52] Schultze, G. R., *J. Am. Chem. Soc.*, **53**, 3561 (1931).

[53] Badger, R. M., and Urmston, J. W., *Proc. Nat. Acad. Sci.*, **16**, 808 (1930); *Chem. Abs*, **25**, 1737 (1931).

[54] Schumacher, H. J., and Wiig, E. O., *Z. physik. Chem.*, **11B**, 45 (1930).

[55] Murthi, D. S. N., *J. Indian Chem. Soc.*, **12**, 173 (1935); *Brit. Chem. Abs.*, **A**, 832 (1935); *Chem Abs.*, **29**, 5351 (1935).

[56] Schumacher, H. J., and Stieger, G., *Z. physik. Chem.*, **12B**, 348 (1931).

[57] Murthi, D. S., *J. Indian Chem. Soc.*, **12**, 173 (1935); *Chem. Abs.*, **29**, 5351 (1935).

[58] Dickinson, R. G., and Nies, N. P., *J. Am. Chem. Soc.*, **57**, 2382 (1935).

[59] Forbes, G. S., and Nelson, A. F., *J. Am. Chem. Soc.*, **58**, 182 (1936).

DeRight and Wiig[61] find that in red light, a solution of iodine and ethylene in carbon tetrachloride readily yields ethylene iodide, although no dark reaction occurs in 36 hours. The rate depends on the ethylene pressure and falls off with decreasing concentrations of iodine. The reaction probably involves excited iodine molecules. The photodecomposition yields iodine atoms, and the sensitized decomposition proceeds similarly.

The photochemical chlorination of acetylene has been investigated by Peters and Neumann[62] under a variety of conditions by static and dynamic methods. When mixtures of chlorine and acetylene at pressures up to 50 mm. were illuminated by a mercury arc, the pressure rose after a definite time, and then dropped suddenly, indicating the formation of $C_2H_2Cl_2$ and $C_2H_2Cl_4$. With higher proportions of acetylene, larger proportions of the former compound were obtained. An increase of 30 per cent in the time of illumination increased the chlorine consumption by 5 per cent. The percentage of contraction on illumination increased with the pressure. Pure nitrogen had little effect on the reaction, but nitrogen containing about 5 per cent of oxygen stopped it. In the presence of a large excess of hydrogen, a smaller yield was obtained but there was practically no formation of hydrogen chloride. The explosive process $C_2H_2 + Cl_2 \rightarrow 2C + 2HCl$ cannot occur at pressures below 70 mm.

The photobromination of acetylene, in which $C_2H_2Br_2$ is formed, has been studied at 150°C. by Booher and Rollefson,[63] using the wave-lengths 4358, 5461 and 5791A. It is a chain reaction with chain length of from about 500 at 150°C. to 3000 at 20°C. independent of the wave-length. The rate depends on the first power of the light intensity and on powers of the bromine and acetylene concentrations between zero and one. No difference is found in the effect of light of wave-lengths above and below the convergence limit of the bromine bands. The influence of temperature is very small.

These experiments were repeated by Franke and Schumacher,[64] who minimized the effects of impurities by using greaseless valves and measured the rate by a spiral quartz pressure gauge. Their results differed, but exact rate equations could not be given. The following reactions were suggested as playing a part in the mechanism:

$$Br_2 + h\nu \longrightarrow Br + Br.$$

$$Br + C_2H_2 \longrightarrow C_2H_2Br$$

$$C_2H_2Br \longrightarrow C_2H_2 + Br$$

$$C_2H_2Br + Br_2 \longrightarrow C_2H_2Br_2 + Br$$

$$C_2H_2Br \longrightarrow W \longrightarrow C_2H_2 + 1/2Br_2$$

$$Br \longrightarrow \text{Wall} \longrightarrow 1/2Br_2$$

$$Br + Br + M \longrightarrow Br_2 + M'$$

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[60] Forbes, G. S., and Nelson, A. F., *J. Am. Chem. Soc.*, **59**, 693 (1937).

[61] DeRight, R. E., and Wiig, E. O., *J. Am. Chem. Soc.*, **58**, 693 (1936).

[62] Peters, K., and Neumann, L., *Angew. Chem.*, **45**, 261 (1932).

[63] Booher, J. E., and Rollefson, G. K., *J. Am. Chem. Soc.*, **56**, 2288 (1934).

[64] Franke, W. K., and Schumacher, H. J., *Z. physik Chem.*, **B34**, 181 (1936); see, however, Rollefson, G. K., *Z. physik. Chem.*, **B37**, 472 (1937).

Higher quantum yields (40,000) have since been found at 90°C. and with 100 mm. pressure of each of the reactants.[65]

The bromination of acetylene bromide, by wave-lengths 5460, 4360 and 4060A, is thirty times as fast in the gas phase as in solution in carbon tetrachloride under equivalent conditions.[66] In both cases, the unimolecular rate constant for the removal of bromine is proportional to the square root of the absorbed energy. The temperature coefficient is 1.4.

Ghosh and Bhattacharya extend the work to include the iodination of phenylacetylene, dicyclopentadiene and β-amylene.[67]

OTHER ALIPHATIC COMPOUNDS

Volmar [68] claimed that methyl sulfate readily undergoes chlorination at ordinary temperatures under the influence of ultraviolet rays and more slowly under the influence of the light from an arc lamp or a metal filament lamp, the product in all cases being methyl chloromethyl sulfate. The fixation of a second chlorine atom was not observed. It was thought to require radiations of such a wave-length that the dichloromethyl sulfate would be decomposed as it formed.

The bromination of ethyl alcohol occurs under the influence of light.[69] The reaction is retarded by potassium bromide. A satisfactory mechanism has not yet been proposed. Berthoud believes C_2H_5O may function as an intermediary. In the case of propyl, isopropyl and butyl alcohols the quantum yields are large (5660, 6800 and 8500A).[70] They increase with temperature and decrease with increasing wave-lengths. The rate of the reaction increases with the amount of light energy-absorbed. At these longer wave-lengths the primary reaction is believed to be the activation of bromine molecules. The temperature coefficients were found to be above two in most cases. With Bhagwat, Malaviya and Dhar [71] found the rate of the reaction with propyl alcohol to be proportional to the square root of the light intensity at 6800A and nearly so at 8500A, but directly proportional to it at 5660A. On the other hand, with isopropyl and butyl alcohols, the rates were proportional to the square root at 6800A and directly proportional to it at 5600 and 8500A. In all cases the reaction is retarded by potassium bromide. and the rates are then proportional to the square roots of the intensities.

The rate of addition of iodine to allyl alcohol in aqueous solution is not influenced by light, but with carbon tetrachloride as solvent there is a photochemical reaction similar to the photobromination.[72]

Monochloropinacolone has been prepared by treating pinacolone in carbon tetrachloride with chlorine in a quartz flask exposed to strong ultraviolet light.

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[65] Müller, K. L., and Schumacher, H J, *Z. physik. Chem.*, **B39**, 352 (1938), **B40**, 318 (1938).

[66] Ghosh, J. C., Bhattacharya, S. K, and Bhattacharya, S. C., *Z. physik. Chem*, **B32**, 145 (1936). For the bromination of dichloroacetylene, Ghosh, J. C., Bhattacharya, S. K, and Murthi, M. L. N., *J. Indian Chem Soc.*, **14**, 425 (1937); *Brit. Chem. Abs.*, **AI**, 627 (1937).

[67] Ghosh, J. C., and Bhattacharya, S. K, *Science and Culture*, **3**, 120 (1937); *Chem. Abs.*, **32**, 414 (1938).

[68] Volmar, *Bull. soc. chim.*, **27**, 181 (1920); *J. Chem. Soc.*, **118**, (I), 661 (1920); *Chem. Abs.*, **14**, 3406 (1920).

[69] Bugarski, S., *Z. physik. Chem.*, **71**, 705 (1910); Berthoud, A., and Béraneck, J., *J. chim. phys.*, **25**, 28 (1928).

[70] Malaviya, K. N., and Dhar, N. R., *Z. anorg. allgem. Chem.*, **199**, 418 (1931); *Chem. Abs.* **25** 5846 (1931).

[71] Bhagwat, W. V., Malaviya, K. N., and Dhar, N. R., *Z. anorg. allgem Chem.*, **199**, 406 (1931); *Chem. Abs.*, **25**, 5846 (1931).

[72] Berthoud, A., and Mosset, M., *J. chim. phys.*, **33**, 272 (1936).

[73] Hill. G. A., and Kropa, E. L., *J. Am. Chem. Soc.*, **55**, 2509 (1933).

It is a highly lachrymatory ketone.[73] Hill and Kropa also find that colorless monobromopinacolone, when exposed for six hours to ultraviolet light, becomes yellow and then orange. Most of the material is unchanged but some dibromopinacolone can be obtained.

Acids and Their Salts. In the manufacture of lethal gases in Germany during the war, Carr [74] states, the preparation of diphosgene proved very troublesome. Methyl formate was chlorinated in vessels furnished with chlorine pipes and carefully lined first with lead and then with two layers of tiles. The cement was said to consist of powdered fireclay, asbestos and sodium silicate. These precautions were necessary because any metal introduced onto the mixture from the reaction vessel acts as an anticatalyst. The temperature had to be carefully controlled during the reaction to obtain the best results. As a source of light, which was necessary, an Osram lamp of 4000 c.p. was used. The reaction took from six to eight days for completion.

In the process of chlorination of methyl chloroformate described by Kling, Florentin, Lassieur and Schmutz,[75] methyl chloroformate is first prepared by the action of carbonyl chloride on methyl alcohol at as low a temperature as possible, a small amount of dimethyl carbonate being formed as a by-product. No matter whether the chlorination takes place in sunlight, arc light, or the light of an incandescent lamp, the monochloroester is obtained almost free from the dichloro-compound which, having almost the same boiling point, is very difficult to remove. Further chlorination gives the dichloroester which is easily fractionated from the trichloroester which is also formed. Chlorination to the limit gives the latter. Methyl formate may also be used as the starting material, giving practically the same products.

Grignard, Rivat and Urbain [76] state that chlorination of methyl chloroformate in diffused light gives only the chloromethyl ester, and that bright sunlight is necessary for the formation of the di- or trichloromethyl ester. In ultraviolet rays, the trichloromethyl ester is easily obtained. The effect of temperature is such that up to 110-112°C. the chlorination proceeds smoothly; from 113-114°C., it slackens very noticeably. At 117°C. decomposition begins to take place, with the formation of carbonyl chloride. Catalysts, such as ferric chloride, antimony chloride, etc., are initially beneficial in the formation of dichloromethyl ester, but when a certain concentration has been reached, decomposition commences, and may continue indefinitely, since some of the perchloride becomes dissolved in the liquid and continues its action.

Formic acid itself is chlorinated with quantum yields of about 2000 when the 3650A mercury lines are employed. These lines do not affect the acid but only the chlorine in the primary process. West and Rollefson [77] find evidence for the production of an unstable intermediary product, chloroformic acid. If this is destroyed by heat or if there is an excess of chlorine, hydrochloric acid and carbon dioxide are the only products. There is no appreciable difference in reactivity between the single and double molecules of formic acid. For the former the reactions involved may be:

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[74] Carr, F. H., *J. Soc. Chem. Ind.*, **38**, 468R (1919).

[75] Kling, A., Florentin, D., Lassieur, A., and Schmutz, R., *Compt rend.*, **169**, 1046 (1919), *Chem Abs.*, **14**, 738 (1920).

[76] Grignard, V., Rivat, G., and Urbain, E., *Compt rend.*, **169**, 1074, 1143 (1919); *J. Chem. Soc.*, **118**, 1138 (1920).

[77] West, H. L., and Rollefson, G. K., *J. Am. Chem. Soc.*, **58**, 2140 (1936).

$$
\begin{aligned}
&Cl_2 + h\nu \longrightarrow Cl + Cl\\
&Cl + HCOOH \longrightarrow COOH + HCl\\
&COOH \longrightarrow CO_2 + H\\
&COOH + Cl_2 \longrightarrow ClCOOH + Cl\\
&H + Cl_2 \longrightarrow HCl + Cl\\
&ClCOOH \longrightarrow CO_2 + HCl\\
&Cl + Cl + M \longrightarrow Cl_2 + M
\end{aligned}
$$

A similar mechanism can be given for the reaction with the double molecules.

In the chlorination of acetic acid in a quartz flask under the influence of rays from an iron arc, Custis [78] found that the yield of monochloracetic acid is improved by the use of red phosphorus as a catalyst. No reaction was observed when the light from an ordinary projection lantern replaced the iron arc. No results were obtained by passing the chlorine gas through a quartz tube irradiated with ultraviolet light before passing it into a non-irradiated flask containing glacial acetic acid.

Benrath and Hertel found that acetyl chloride and isobutyric acid behave similarly to acetic acid. With propionic acid and with ethyl malonate, the reaction commenced slowly and then continued at a rate proportional to the time until one atom of hydrogen had been replaced. The second atom then reacted at a much slower rate and in accordance with the logarithmic law. Two atoms of hydrogen were replaced in *n*-butyric acid, both at logarithmic rates, the steps of the reaction being markedly distinct. The chlorination of ethyl ether proceeded linearly during the displacement of one atom and then, after slowing up, the second atom was replaced at a logarithmic rate. The induction period was long in the case of acetic anhydride and the reaction was in two phases, but the rates were neither linear nor logarithmic. Some of the results indicated a tendency toward periodicity.[79]

In the photobromination of lactic acid, Ghosh and Basu [80] found it impossible to get regular values for a monomolecular rate constant. It appeared that the quantum yield was low, about 0.25, but the measurements were not considered very accurate since about two-thirds of the transformation appeared to be due to the thermal reaction. Much more regular results were obtained in the case of calcium lactate, but even in this case the dark reaction accounted for about 75 per cent of the observed velocity. Increasing the concentration of the salt increased the velocity constant, but increasing the bromine concentration made the constants irregular, the reaction tending to degenerate into one of zero order. When the concentration of the salt is small (0.03N), the quantum yield is about 0.5, but this becomes unity when the concentration is increased to 0.06N.[81]

Purkayastha [82] finds that in the bromination of organic acids, there is an induction period which vanishes in the presence of potassium bromide. The quantum yields, higher than those of other observers, possibly because of elimination of oxygen, are for light of 4700A, 15 (lactic acid), 13 (phenyl-lactic acid), 13 (mandelic acid) and 3 (citric acid). The induction period is ascribed to the formation of complexes between bromine and the reacting acid. The velocity constants vary inversely with the square root of the incident intensity of the blue light. At 5420, 4880, 4480, 4080 or 3650A, the order is zero molecular.

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[78] Custis, H. H, *J Frank Inst*, **184,** 874 (1917), see also Benrath, A., and Hertel, E., *Z. wiss. Phot.*, **23,** 30 (1924)

[79] See, however, Plotnikow, J., *Z. wiss. Phot.*, 2379 (1924).

[80] Ghosh, J. C, and Basu, K., *Quart. J. Indian Chem. Soc.*, **2,** 39 (1925); *Chem. Abs*, **20,** 43 (1926).

[81] For temperature coefficients in various solvents, see Yajnik, N. A., and Uppal, H. L., *J. Indian Chem. Soc.*, **6,** 729 (1929); *Chem Abs.*, **24,** 1035 (1930).

[82] Purkayastha, R M, *J. Indian Chem. Soc*, **6,** 361, 375, 385 (1929); **7,** 991 (1930); *Chem. Abs.*, **23,** 5420 (1929); **24,** 784 (1930); **25,** 2922 (1931).

In the case of the bromination of tartaric acid in aqueous solution, the Indian workers[83] found an induction period of two days. The unimolecular rate constant decreased as the initial concentration of bromine was increased, and increased with that of tartaric acid, the more so when part of the acid was replaced by the acid salt. It diminished when hydrobromic acid was added before exposure, decreased with time and increased rapidly with increase in frequency of light employed. It varied approximately as the square root of the light intensity. The quantum yield was high, bromine atoms being involved in the mechanism. These reacted with oxygen (present in solution or liberated by the photochemical reaction of bromine molecules with water) at a rate directly proportional to the oxygen concentration and to the square of the bromine atom concentration. Photoinhibitors were also destroyed by reacting with bromine atoms. The temperature coefficient of the velocity is high, 4.6 per 10°C.

Prik[84] chlorinated impure methyl stearate in diffused light without a catalyst until it contained 2.5 atoms of chlorine per molecule. When heated to 100°C. with zinc dust, this product split off 12 per cent of its chlorine.

The reactions of bromine and of iodine with oxalic acid have been discussed in Chapter 22. In the case of the chlorination by wave-lengths 4650, 5650, and 7304A, Bhattacharya and Dhar[85] find the temperature coefficients to be 2.3, 2.4 and 2.5. The quantum yields are 8.6, 7.2 and 4.9, there being little difference in the reaction as conducted by absorption in the band or continuous spectral regions. In a later reinvestigation of this reaction, they, with Mukerji,[86] concluded that in the absence of potassium iodide the thermal and the photochemical reactions are uni- and semi-molecular, respectively. The reaction rate is not a constant function of the light intensity. Stirring increases the rate and reduces the temperature coefficient, which is the smaller the greater the acceleration due to light.

The addition of bromine to maleic and fumaric acids is not influenced by light, according to Berthoud and Mosset.[87]

When bromine was added to β-phenylpropiolic acid in cold chloroform and the reaction allowed to go to completion at room temperature in light, the *cis-trans* ratio in the products was about two to one. In darkness at zero, it was three to two. With the methyl ester, the ratios were one to three and one to two, respectively.[88]

In preparing α-bromo-β-methoxybutyric acids, West and Carter brominate in sunlight an addition product of crotonic acid and mercuric acetate.[89]

Cyclic Compounds. Mono- and di-brom-phenylcyclopropane-1,2-dicarboxylic acids were prepared by Haerdi and Thorpe[90] by using the rays of a powerful arc lamp. Nicolet and Sattler[91] found that bromine reacts easily with ethylcyclopropane-1,1-dicarboxylate even in diffused light. The nature of the product depended on the conditions of bromination. Apparently both ethyl 2-bromocyclopropane-1,1-dicarboxylate and β-bromoethylbromomalonate were formed in all cases, but the proportion of the latter was much higher when the bromination was carried out at higher temperatures and under mercury-arc illumination. The former is apparently the primary product from which the latter is produced by subsequent reaction of the hydrobromic acid liberated. Bromination of cyclopropane-1,1-dicarboxylic acid in carbon tetrachloride in ultraviolet light affords bromo-β-bromoethylmalonic acid. In chloroform, the product is a viscous oil, which loses carbon dioxide upon distillation with the formation of 2-bromocyclopropane-carboxylic acid. Bromination of ethyl 1-cyanocyclopropane-1-carboxylate affords ethyl 2-bromo-1-cyancyclopropane-1-carboxylate and ethyl α,γ-dibromo-α-cyanobutyrate. Bromine is without action in ultraviolet light on cyanocyclopropane and 1-cyanocyclopropane-1-carboxylic acid.

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[83] Ghosh, J. C., and Mukherjee, J., *Quart J. Indian Chem. Soc.*, **2,** 165 (1925); *Chem. Abs.*, **20,** 870 (1926); Ghosh, J. C, and Basu, K., *J. Indian Chem. Soc.*, **5,** 343, 361 (1928); *Chem. Abs.*, **22,** 4379 (1928).

[84] Prik, E. M, *Plasticheskie Massui*, **6,** 26 (1934), *Chem. Abs.*, **29,** 4734 (1935); see also Scheibler, H., and Schmidt, H. J, *Ber*, **69B,** 12 (1936).

[85] Bhattacharya, A. K, and Dhar, N. R., *J. chim. phys.*, **26,** 556 (1929).

[86] Bhattacharya, A. K., Dhar, N R., and Mukerji, B. K., *J. Indian Chem. Soc.*, **12,** 151 (1935); *Brit. Chem. Abs.*, **1935A,** 832.

[87] Berthoud, A., and Mosset, M, *J. chim phys*, **33,** 272 (1936)

[88] Ayyar, P. R., *J. Indian Inst Sci*, **18A,** 123 (1935); *Chem. Abs.*, **30,** 2185 (1936).

[89] West, H. D., and Carter, H. E., *J Biol. Chem.*, **119,** 103 (1937).

[90] Haerdi, W., and Thorpe, J. F., *J. Chem. Soc.*, **127,** 1237 (1925).

[91] Nicolet, B. H., and Sattler, L., *J. Am. Chem. Soc.*, **49,** 2069 (1927).

The photobromination of cyclohexane by rays of wave-length 5460A at 30°C. has been investigated by Wood and Rideal.[92] Both the thermal and the photochemical reactions conform to the unimolecular law and the latter has no temperature coefficient. The velocity of the reaction is proportional to the light intensity, independent of the cyclohexane concentration and reduced by the presence of oxygen, the inhibition by the latter being independent of the pressure of the cyclohexane. Jost [93] found the characteristics of the reaction to be the same in both the regions of continuous and discontinuous absorption by the halogen. The reaction constant varied approximately with the square root of the cyclohexane concentration. The temperature coefficient was two and the quantum yields increased with rising temperatures.

In carbon tetrachloride, the chlorination of this compound under the influence of either white or monochromatic light, is unimolecular with respect to chlorine. The velocity coefficient is directly proportional to the intensity of the incident radiation, independent of the concentration of chlorine and increases slightly with the concentration of the cyclohexane.[94] The coefficient diminishes a little as the reaction proceeds, apparently because of the retarding influence of the chlorcyclohexane formed. The quantum efficiency is 19 at 4360A, 30 at 4040A and 41 at 3660A. The temperature coefficients for these wave-lengths are 1.5, 1.29 and 1.26, respectively.

AROMATIC COMPOUNDS

The influence of light in facilitating the chlorination of toluene in the side-chain has long been known and employed in practice. Before discussing this reaction and its application, attention will be devoted to the halogenation reactions of benzene.

Luther and Goldberg [95] found the frequently irregular course of the photochlorination of benzene to be due to the retarding effect of small quantities of oxygen, an effect frequently noted in chlorination reactions in general. The rate of the reaction with liquid benzene is proportional to the square of the pressure of the chlorine employed. The final product seems to be largely benzene hexachloride.[96]

On the other hand, in the vapor phase the reaction proceeds by a *short*-chain mechanism.[97] It was found that the main initial reaction is one of addition but that some substitution also occurs. At the beginning, the rate of change of pressure is proportional to the square root of the light intensity and to the pressure of the chlorine and that of the benzene. No pressure change is observed unless phenyl chloride forms and condenses on the wall. After this there is a liquid reaction which consists in large part in the addition of chlorine to benzene dissolved in the liquefied phenyl chloride.

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[92] Wood, B. J., and Rideal, E. K., *J. Chem. Soc.*, 2466 (1927).

[93] Jost, W., *Z. physik. Chem., Bodenstein Festschrift*, 291 (1931).

[94] Basu, K. P., *J. Indian Chem. Soc.*, **6**, 691 (1929); *Chem. Abs.*, **24**, 1033 (1930).

[95] Luther, R., and Goldberg, E., *Z. physik. Chem.*, **56**, 43 (1906); *J. Chem. Soc.*, **90**, *(II)*, 641 (1906).

[96] Slator, A., *Z. physik. Chem.*, **45**, 540 (1903).

In the gas phase photochlorination of chlorobenzene, which also proceeds by short chains, the initial rate of reaction of the chlorine is proportional to a power of the light intensity between 0.5 and 1.0. The rate is also about proportional to the product of the chlorine and chlorobenzene concentrations and is increased by surfaces. The ratio of substitution to addition increases from much less than one to more than one as the ratio of chlorine used to the initial pressure of chlorobenzene increases. The rate of addition of chlorine to *p*-dichlorobenzene is slightly less than that to chlorobenzene. Some intermediate substances have been isolated; the final product is dodecachlorocyclohexane.

There is little difference in the rates of photochemical chlorination of the three dichlorobenzenes.[98] The rate is proportional to the light intensity at low intensities but at higher ones depends on some power between 0.5 and 1.0. It is independent of the chlorine pressure except as this affects the light absorption, but is proportional to the pressure of dichlorobenzene.

The rate of addition of liquid chlorine to three trichlorobenzenes in sunlight at room temperature has been found by van der Linden [99] to decrease in the order of the 1,2,3-, 1,2,4- and 1,3,5- compounds, requiring 7 days, 10 days and 9 weeks, respectively. The first gives only one isomer of 1,1′,2,2′,3,3′,4,5,6-nonachlorocyclohexane, of musty camphor-like odor, m.p. 80°C. The second gives a series of mixed crystals of two isomers of $C_6H_3Cl_9$ and 1,2,2′,3,4,4′,5,6-octachloro-6-cyclohexene, obtained by the loss of hydrogen chloride from a third unstable isomer. The 1,3,5-trichlorobenzene yields one isomer of 1,1′,2,3,3′,4,5,5′,6-nonachlorocyclohexane. Addition is assumed to occur most readily at double linkings unsubstituted in both Kekule forms. Van der Linden also reports [100] on the addition of chlorine to penta- and hexachlorobenzene. The former yielded hexachlorobenzene and a mixture of 1,2,3,3′,4,4′,5,6,6′-*ennea*chloro-1-cyclohexene and its stereoisomer. The hexachlorobenzene gave dodecachlorocyclohexane and a small quantity of decachlorocyclohexene.

The *β*-isomer of hexachlorobenzene after 17 days in sunlight, formed principally *β*-*p*-dichlorobenzene hexachloride and probably the 1,2,4-trichlorine derivative.[101]

Hexabromodihydrobenzene and liquid chlorine, exposed to sunlight for 40 days in a sealed tube, gave dodecachlorohexane, $C_6H_2C_{12}$, melting 108-110°C.[102]

The liquid phase photobromination of benzene in carbon tetrachloride by low concentrations of bromine (1 to 2 mg. per cc.) has been studied by Meidinger.[103] The bromine can either be directly substituted in the ring with the formation of monobromobenzene, or the double bonds may be broken with the formation of benzene hexabromide. The reaction is independent of the bromine concentration and of the wave-length of light used. Meidinger was unable to explain his observation that the temperature coefficient decreased from 1.6 to 1.0 as the concentration of benzene employed decreased.

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[97] Lane, C. E., Jr., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **54**, 161 (1932); Smith, H. P, Noyes, W. A, Jr., and Hart, E. J., *Ibid.*, **55**, 4444 (1933); Hart, E J, and Noyes, W. A., Jr., *Ibid*, **56**, 1305 (1934).

[98] Fisk, C. F., and Noyes, W. A., Jr., *J. Am. Chem. Soc.*, **58**, 1707 (1936).

[99] van der Linden, T., *Rec. trav. chim.*, **55**, 315 (1936); *Chem. Abs*, **30**, 6345 (1936).

[100] van der Linden, T., *Rec. trav. chim.*, **55**, 569 (1936); *Chem. Abs.*, **30**, 7103 (1936).

[101] van der Linden, T., *Rec. trav. chim.*, **57**, 217 (1938); *Chem. Abs.*, **32**, 4542 (1938).

[102] van der Linden, T., *Ibid.*, **57**, 401 (1938); *Chem. Abs.*, **32**, 5775 (1938).

[103] Meidinger, W., *Z. physik, Chem.*, **5B**, 29 (1929); *Z. Elektrochem.*, **35**, 738 (199).

Rabinowitsch[104] also found the temperature coefficient 1.6; it varied but little with the light intensity or the wave-length between 3000 and 5500A. There was, however, a fall with wave-lengths approaching the convergence limit of bromine and an increase with increasing concentrations of the latter. The quantum yield at room temperature was 0.4 to 0.9. This author believed that even when the solution was considerably diluted with solvent, the bromine molecules remained attached to the benzene molecules and on light absorption reacted with them. The compound $C_6H_6Br_6$ may be formed chiefly by the reaction of activated bromine molecules, but the phenyl bromide results from a reaction with bromine atoms:

$$C_6H_6 + Br \longrightarrow C_6H_5 + HBr$$
$$C_6H_5 + Br_2 \longrightarrow C_6H_5Br + Br.$$

The first of these requires thermal activation and accounts for the high temperature coefficient of the photochemical reaction and the lessening of the coefficient on dilution.

In a sealed tube exposed to light, phenyl fluoride and liquid chlorine react vigorously, yielding in a day a few crystals, possibly 1-fluoro-1,2,3,4,4′,5,6-heptachlorocyclohexane[105] and an oil which on steam distillation yielded a volatile oil, $C_6H_5FCl_6$, and a non-volatile residue, probably a mixture of isomers of this composition. Under similar conditions, phenyl bromide liberated bromine and hydrogen chloride and formed a chlorobromobenzene hexachloride. Phenyl iodide reacted much more slowly; among the products isolated after several weeks were C_6ICl_5, p-ClC_6H_4I and probably 2,4,5-trichloroiodobenzene.

Toluene. According to Book and Eggert,[106] toluene, chlorinated by a stream of chlorine at 105° to 110°C., yields almost exclusively benzyl chloride, irrespective of whether the reaction is carried out in light or in darkness, provided a chlorine "carrier," *e.g.*, ferric chloride, is not present. In the presence of such a "carrier," however, considerable amounts of *o*- and *p*-chlorotoluene are produced. At −80°C. a photochemical reaction occurs in the absence of a carrier as a result of absorption of the orange and light green mercury lines, with a quantum yield of about 25. The initial reaction probably comprises the formation of hydrogen chloride together with chlorotoluene or benzyl chloride.

The influence of light on the chlorination of toluene has been the subject of several early patents.[107]

In the laboratory of the senior author,[108] a number of experiments have been made to compare the production of benzyl chloride, benzal chloride and benzotrichloride under various conditions. The best results were obtained by passing an excess of toluene vapor mixed with chlorine through a transparent quartz tube at variously elevated temperatures and exposed to ultraviolet radiations. The product was withdrawn from the reaction tube and the contents collected and fractionated; the unused toluene was returned through the reaction tube. In order to determine the effect of ultraviolet rays on this reaction the source of the rays was removed and the experiment carried out in a similar manner. The results of one test are given in Table 22.

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[104] Rabinowitsch, E., *Z. physik. Chem*, **19B** 190 (193).

[105] van der Linden, T., *Rec. trav. chim.*, **55**, 282 (1936); *Chem. Abs.*, **30**, 5192 (1936).

[106] Book, G., and Eggert, J., *Z. Elektrochem.*, **29**, 521 (1923); *Ber.*, **59B**, 1192 (1926); *Chem. Abs*, **18**, 668 (1924); See also Bergel, F., *Ber.*, **59B**, 153 (1926); *Chem Abs*, **20**, 1602 (1926)

[107] See, *e.g.*, Ransford, R. B., British P. 16,317, July 8, 1914; *J. Soc. Chem. Ind.*, 1203 **(1915)**.

[108] Ellis, Carleton, U. S. P. 1,202,040, Oct. 24, 1916; for a special form of chlorination chamber, Ellis, Carleton, U. S. P. 1,146,142, July 13, 1915.

Table 22.—Products from Chlorination of Toluene.

Fraction	Quartz Tube without Ultraviolet	Quartz Tube with Ultraviolet
	per cent	
Up to 150°C.	72	42
150-170°C.	4.2	2.
170-185°C.	18.5	47.5
185-215°C.	3.8	6.5

A process for the manufacture of side-chain chlorinated toluene advocated by Gibbs and Geiger,[109] called for ultraviolet radiation. It was claimed that when toluene in vapor phase is mixed with chlorine gas in the definite theoretical proportions to produce chlorinated side-chain products and the mixture exposed to ultraviolet rays, the bodies desired are produced in greatly increased yields and without the production of interfering by-products. By carefully regulating the speed at which the reacting substances pass continuously through the reaction chamber, a high degree of purity results. They state that it is advisable to work without a catalyst since it is not essential to the reaction and would tend to contaminate the products. According to this process, benzyl chloride, benzal chloride and benzotrichloride may be produced in accordance with the proportion of chlorine employed. Gibbs [110] states that when a low-pressure mercury-vapor lamp is used, a mixture of benzyl chloride and benzal chloride is produced and that a high-pressure mercury-vapor lamp gives benzotrichloride. Conklin [111] has patented sectional glass reaction towers for the chlorination of benzene or toluene under the influence of actinic rays. However, the use of ultraviolet rays is not essential.[112]

In experiments on the photobromination of toluene, made in atmospheres of 96 per cent and 4 per cent nitrogen, LeBlanc and Andrich [113] found the yield of benzyl bromide independent of the intensity of light and constant throughout the entire portion of the spectrum investigated. The speed of the reaction decreased with decrease of wave-length and was practically zero for wave-lengths shorter than 3000A. Swensson [114] reports that the rate of absorption of bromine by toluene and xylene in the presence of alcohol and when exposed to the rays of a quartz mercury arc at 20°C. is retarded, owing to the ability of alcohol to remove the hydrogen bromide, which catalyses the reaction, at the same time being itself decomposed. Kharasch, White and Mayo [115] believe that in light the yield of the side-chain bromination reaction is lowered when oxygen is partly excluded. They consider it a chain reaction carried by bromine atoms, the source of which may be hydrogen bromide when oxygen or oxygen carriers are present.

Natelson [116] obtained an 85-per cent yield of $C_6H_5CHClCH_3$ based on the chlorine employed from ethylbenzene in the light of an S-1 sun-lamp. Evans, Mabbott and Turner[117] found chlorination of pure ethylbenzene in diffused daylight to yield a mixture of α- and β-phenylethylchlorides, increased illumination increasing the proportion of the former. In experiments of Varma, Sahay and Subramonium,[118] the addition of eight drops of nitrosulfonic acid and two cc. of bromine in ten cc. of acetic acid to ten cc. of ethylbenzene in bright sunlight yielded a small quantity of 4-bromoethylbenzene and four grams of α-bromoethylbenzene. The former product was obtained in greater yield in the absence of light. Bromination of ten cc. of 4-chloroethylbenzene in bright sunlight produced seven cc. of 4-chloro-α-bromoethylbenzene.

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[109] Gibbs, H. D., and Geiger, G. A., U. S. P. 1,246,739, Nov. 13, 1917; Canadian P. 186,466, Sept. 10, 1918.

[110] Selden Co. and Gibbs, H D., British P. 123,341, Oct 22, 1927; *Chem. Abs*, **13**, 1478 (1919); *J. Soc. Chem. Ind*, **38**, 268A (1919).

[111] Conklin, E. P., U S. P. 1,828 859, Oct. 27, 1931, to Solvay Process Co., *Chem. Abs.*, **26**, 632 (1932).

[112] Silberrad, O., and Boake, A., [British P. 259,329, July 22, 1925; *Chem. Abs.*, **21**, 3370 (1927)] chlorinated organic compounds with sulfuryl chloride in the presence of catalysts such as chlorides of phosphorus, manganese, arsenic, selenium, antimony, bismuth, molybdenum, and the chlorides of iron, sulfur and aluminum. Actinic light may be used.

[113] LeBlanc, M., and Andrich, K., *Z. Elektrochem*, **20**, 543 (1914)

[114] Swensson, T., *Z. wiss. Phot.*, **20**, 206 (1921), *J. Chem. Soc.*, **120**, II, 291 (1921).

[115] Kharasch, M. S., White, P. C., and Mayo, F. R., *J. Org. Chem.*, **3**, 33 (1938).

[116] Natelson, S., *Ind. Eng. Chem.*, **25**, 1391 (1933).

Intense visible light causes a rapid reaction between cyclopropane and bromine vapor. About two per cent of the bromine reacted appears as hydrogen bromide. The main product is $BrCH_2CH_2CH_2Br$.[119]

For the laboratory-scale preparation of *m*-xylylchloride by the chlorination of *m*-xylene with the production of as little 4-chloro-1,3-dimethylbenzene as possible, King and Merriam[120] developed a chlorinator made from a 500-cc. distilling flask and a Pyrex tube connected to a reflux condenser. It was illuminated by a 400-watt nitrogen-filled lamp while 260 gms. of *m*-xylene was boiled in the flask. Chlorine (126 gm.) was passed in at the rate of 40 gms. per hour through a 0.5 mm. tube directly into the current of vapor. 17 gms. of *m*-xylene was found remaining in the hydrogen chloride absorbers and 305 gms. of product was in the flask. As a result of very careful fractionation, 68.79 gms. of *m*-xylene was recovered and 20.20 gms. of 4-chloro-1,3-dimethylbenzene and 190.83 gms. of *m*-xylyl chloride were obtained. In the presence of oxygen, chlorination was extremely slow.

The influence of ultraviolet radiation, in the presence and absence of catalysts, on the reactivity of halogen bound to a carbon ring, has been investigated by Rosenmund, Luxat and Tiedemann.[121] The comparative inertness of a halogen in an aromatic compound is overcome in the presence of copper at 180 to 220°C. At somewhat lower temperatures, the radiation from a quartz mercury-vapor lamp has a decidedly accelerating effect on the reaction

$$ClC_6H_4COOH + KOH \longrightarrow HOC_6H_4COOH + KCl$$

in the absence of copper and is still more active in its presence. At 104°C., the radiation is still an accelerating agent, but the copper is inactive.

According to Olivier,[122] when *p*-chlorobenzene sulfochloride in ethereal solution is exposed to direct sunlight or to the rays of a Uviol lamp, chlorine is liberated and oxidation takes place with the formation of the free sulfonic acid. When the experiment is carried out by passing dry oxygen through the ethereal solution of the sulfochloride while exposed to the rays of the lamp, the quantity of chlorine collected shows a deficit when compared with the equivalent of sulfonic acid formed; aldehyde and hydrochloric acid are found in the aqueous liquid on treatment with water. It is probable, therefore, that some of the chlorine reacts with the ether to form chloroethyl ether, which is subsequently hydrolyzed to aldehyde. Under favorable conditions, the decomposition of the sulfochloride under the influence of light and oxygen amounts to over 40 per cent in six hours, and the reaction is practically inhibited in the absence of light or oxygen and a peroxide may play a part in the reaction. The presence or absence of moisture has no appreciable influence. The photochemical decomposition of the sulfochloride is considerable in ethereal solution but only slight in chloroform. In benzene and carbon tetrachloride, the reaction does not take place. Other sulfochlorides of the benzene series behave in a similar manner but to a lesser degree.

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[117] Evans, E. B., Mabbott, E. E., and Turner, E. E., *J. Chem. Soc.*, 1159 **(1927)**.

[118] Varma, P. S., Sahay, V., and Subramonium, B. R., *J. Indian Chem. Soc.*, **14**, 157 (1937); *Chem. Abs.*, **31**, 7411 (1937).

[119] Ogg, R. A., Jr., and Priest, W. J., *J. Am. Chem. Soc.*, **60**, 217 (1938).

[120] King, H S., and Merriam, M. K., *Proc. Nova Scotian Inst. Sci.*, **18**, 276 (1933-4); *Chem. Abs.*, **29**, 6214 (1935).

[121] Rosenmund, K. W., Luxat, K., and Tiedemann, W., *Ber.*, **56B**, 1950 (1923); *Chem. Abs.*, 17, 3837 (1923).

[122] Olivier, S. C. J., *Rec. trav. chim.*, **36**, 117 (1916); *J. Soc. Chem. Ind.*, **35**, 1149 (1916).

Schmitz and Co.[123] have prepared esters of phenol homologs halogenated in the side-chain by treating the esters alone or in suitable solvents, such as carbon tetrachloride, with halogen in the presence of light, especially from a source rich in ultraviolet rays.

Jenkins[124] employs a 500-watt tungsten lamp in the conversion of ketones of the type $R'.CH_2COR$ and $R.CH_2COR'$ into α-bromo- derivatives such as R'CHBrCOR and RCHBrCOR'. Feist[125] finds that *p*-acetyltoluene in the light of a mercury lamp at 100 to 110°C. adds six atoms of chlorine, forming *p*-trichloroacetyl trichloromethyl benzene. According to Connerade,[126] the chlorination of dimethylbenzophenone first at 120°C. and then at 140°C., yields, besides products chlorinated in the ring, $(Cl_2CHC_6H_4)_2CO$, a liquid freezing to a crystalline paste at about 0°C. It is very sensitive to light, which transforms it into a plastic mass.

According to I. G. Farbenindustrie,[127] 2,5-dimethyl-4-chlorobenzophenone may be chlorinated by trichlorobenzene at 170-180°C. while being exposed to the action of a mercury-vapor lamp to give an ω-hexachloro- derivative.

Van der Linden[128] has obtained, after chlorination of benzoic acid in sunlight, a γ- and a β-hexachloride, a pentachlorocyclohexene carboxylic acid and a mixture which, when distilled in steam, yielded the first two of these, the α-isomer, 1,2,4,5-tetra-, penta- and hexachlorobenzene and pentachlorocyclohexene carboxylic acid.[129] He found also that benzoyl chloride and chlorine in sunlight slowly gave a mixture of equal parts of δ-1,2,3,4,5,6-hexachlorocyclohexane carboxylchloride and β-1,2,3,4,5,6,4'-heptachlorocyclohexane carboxylchloride, a γ-isomer of the δ-compound, an α-isomer of the β-compound and an oil which, after treatment with dilute alkali and steam distillation yielded a little 1,2,4,5,-tetrachlorbenzene, three isomeric hexachlorocyclohexenes, a mixture of $C_6H_{11}COOH$ and $HOC_6H_4Cl_6COOH$ or of $HOC_6H_5Cl_5COOH$ and $C_6H_5Cl_6COOH$, the acid of the δ-carboxylchloride and ϵ-benzoic acid hexachloride.

Perkin and Stone[130] find that when 2,4-dimethyl benzoyl chloride is brominated at 160°C. by the aid of a mercury lamp, the bromo-acid bromide distilling at 169-171°C. at 15 mm., consists mainly of 2-bromomethyl 4-methyl benzoylbromide, $CH_3C_6H_3(CH_2Br)COBr$, but the fraction 160-180°C. at 15 mm., contains this substance and 4-bromomethyl 2-methylbenzoyl bromide, $CH_2BrC_6H_3CH_3COBr$, in the proportion of about 85 to 15 per cent. When 2,4-dimethylbenzoyl chloride is treated with a calculated amount of chlorine for the introduction of three atoms, at a temperature rising from 180 to 210°C. and in ultraviolet light, and the product is distilled, a fraction is obtained boiling 184-186°C. (16 mm.), the chlorine content of which corresponds to that of the expected ω-trichloro-2,4-dimethyl benzoyl chloride. It was found, however, that this fraction was in reality an almost constant boiling mixture of di- and tetra-chlorinated dimethylbenzoyl chloride. When the chlorination was continued in ultraviolet light until the increased weight corresponded to the introduction of four atoms of chlorine, and the product fractionated, 2,4-di(dichloromethyl)benzoyl chloride, boiling at 192-193°C. (10 mm.) was obtained in good yield. An acid chloride fraction boiling 188-192°C. (14 mm.) was obtained when chlorine was passed into 2,4-dimethyl benzoyl chloride in the presence of ultraviolet light at 200°C. until the increase in weight corresponded to the absorption of five atoms of chlorine. The product contained about equal quantities of the isomeric chlorides, $CCl_3C_6H_3(CHCl_2)COCl$ and $CHCl_2(CCl_3)COCl$. It was also possible to obtain the chloride of 2,4-di(trichloromethyl)benzoic acid by chlorinating at 220°C. in ultraviolet light until six chlorine atoms were absorbed. The yield was 70 to 80 per cent.

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[123] British P. 3053, Feb. 5, 1914, to Schmitz and Co.

[124] Jenkins, S. S., *J. Am. Chem. Soc.*, **56**, 682 (1934).

[125] Feist, F., *Ber*, **67B**, 938 (1934).

[126] Connerade, E., *Bull soc. chim. Belg.*, **43**, 447 (1934); *Chem Abs.*, **29**, 768 (1935).

[127] British P. 394,990, June 29, 1933, to I. G. Farbenind. A.-G.; *Chem Abs.*, **28**, 176 (1934).

[128] van der Linden, T., *Rec. trav. chim.*, **53**, 703, 779 (1934); *Chem. Abs.*, **28**, 5425 (1934).

[129] See also for the chlorination of aromatic carboxylic acids in sunlight, Feist, F., German P. 563,129, May 21, 1930, to I. G. Farbenind. A.-G.

[130] Perkin, W. H., Jr., and Stone, J. F. S., *J. Chem. Soc.*, **127**, 2275 (1925).

The bromination of salicyclic acid to the dibromo- derivative occurs slowly in carbon tetrachloride either in daylight or darkness, and more rapidly in methyl alcohol; but exposure to daylight or to the light of a mercury-vapor lamp scarcely accelerates the reaction.[131]

Austin and Bousquet [132] cause phthalide to react with a rapid flow of chlorine in ultraviolet light at 130-140°C. with vigorous agitation, until approximately 0.75 atom of chlorine per molecule is absorbed. The chlorination product, on hydrolysis with boiling water, followed by cooling, filtering and recrystallizing from benzene, yields phthaldehydic acid. Similarly, a 5-nitro- acid may be formed from 5-nitrophthalide.

Matthews, Bliss and Elder [133] have found that styrolene may be prepared from β-bromohydrocinnamic acid by the action of steam, by a silent electric discharge or by ultraviolet rays.

In the bromination of stilbene in carbon tetrachloride, the velocity coefficient is independent of the concentration of the bromine, but increases as the initial concentration of the stilbene increases. The temperature coefficient is 2.6. The quantum yield is 305 molecules of stilbene dibromide per absorbed quantum.[134]

In direct sunlight or artificial light (but not in darkness in the absence of peroxidic substances), a solution of isostilbene in benzene is transformed by the action of hydrogen bromide into stilbene in about five minutes. The reaction is prevented by antioxidants. It cannot be effected by the use of hydrogen chloride.[135]

According to Ghosh and Basu,[136] the photobromination of ethyl *m*-nitrobenzylidene malonate to the dibromide in carbon tetrachloride solution is reversible. The equilibrium constant varies with the intensity of the light. A rise in temperature causes a slight increase in the concentration of the dibromide. The velocity of the direct action is not affected by the concentration of ester, bromine or dibromide. With Bhattacharya, these authors [137] found an analogous behavior in carbon disulfide, but the values for the equilibrium constant were but one-seventh of those in the former solvent. The velocity of the initial stage was proportional to the concentration of bromine and increased considerably with increase in concentration of the ester.

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[131] Kaufmann, H. P., and Hansen-Schmidy, E., *Archiv Pharm.*, **263**, 32 (1925).

[132] Austin, P. R., and Bousquet, E. W., U. S. P. 2,047,946, to E. I. du Pont de Nemours & Co., *Chem Abs.*, **30**, 6011 (1936); *Brit. Chem. Abs.*, **B**, 879 (1937)

[133] Matthews, F. E., Bliss, H. J. W., and Elder, H. M., British P. 16,828, July 22, 1913.

[134] Ghosh, J. C., and Purkayastha, R. M., *J. Indian Chem. Soc.*, **2**, 261 (1925); **4**, 553 (1927); *Chem. Abs.*, **20**, 1953 (1926); **22**, 4379 (1928). See also Kato, S., *Bull Inst. Phys.-Chem. Research (Tokyo)*, **11**, 765 (1932); *Chem. Abs.*, **26**, 5260 (1932). Quite different results have been reported by Berthoud [138] and coworkers.

[135] Kharasch, M. S., Mansfield, J. V., and Mayo, F. R., *J. Am. Chem. Soc.*, **59**, 1155 (1937).

[136] Ghosh, J. C., and Basu, K. P., *J. Indian Chem. Soc.*, **4**, 375 (1927); *Brit. Chem. Abs.*, **1928 AI**, 176.

[137] Bhattacharya, S. C., Ghosh, J. C., and Basu, K. P., *J. Indian Chem. Soc.*, **5**, 183 (1928); *Brit. Chem. Abs.*, **1928A**, II, 757.

The rate of the addition in chloroform, measured under conditions in which the back reaction is negligible, follows the same laws as the photobromination of cinnamic acid and stilbene.[138]

Tetrachloroarsine, $RAsX_4$, was found by Hamilton and King[139] to decompose into RX and AsX_3 under the influence of ultraviolet light at temperatures of 75 to 120°C. At temperatures around 100°C. the orange-colored 4-methyl phenyl-tetrachloroarsine suddenly decomposed into *p*-chlorotoluene and arsenic trichloride after having been exposed to the radiations for about two hours. With continued chlorination at the same temperature and in the presence of ultraviolet light, there was a rapid gain in weight, indicating that the *p*-chlorotoluene was being chlorinated. Use may be made of the ability of ultraviolet light to break an arsenic-to-carbon linkage in determination of the structure of more complex arsenicals. It was found in the case of *p*-toluene arsenic acid that chlorine substituted in the nucleus and not in the sidechain. In order to prove the position of the chlorine in the ring the arsenic acid was converted into the corresponding tetrachloroarsine, the arsenic-to-carbon linkage broken by the action of chlorine under the influence of ultraviolet light, and the dichlorotoluene thus formed was chlorinated and hydrolyzed to yield 2,4-dichlorobenzoic acid.

HALOGENATION OF OTHER TYPES OF COMPOUNDS

Ultraviolet light has been suggested as an aid in the preparation of chloronaphthalene.[140] According to Davies and Oxford,[141] 4,1-nitromethyl naphthalene and bromine when exposed in a quartz flask to ultraviolet light give a yellow monobromo- derivative, melting at 137.5 to 138.5°C and a very small quantity of a tetrabromo- derivative, melting at 189 to 190°C. The bromination of naphthalene is a unimolecular reaction having a temperature coefficient of 1.57 per ten degrees between 5 and 30°C., according to Kozak and Pazdor.[142] The velocity for a given rate of absorption of energy is greatest in blue light. The velocity of photobromination of various methyl and ethyl derivatives of naphthalene has also a maximum in blue light, but with the bromine substitution reactions of these substances, and also of toluene, there is a secondary maximum in the yellow range.

1,5-dibenzoyl-2,6-dimethyl, 1,5-di(*o*-chlorobenzoyl) and 1,5-di(2,5-dichlorbenzoyl)-2,6-dichloronaphthalene are chlorinated at from 160 to 200°C. with a finely divided stream of chlorine in the light of a mercury lamp to give the ω-hexachloro- derivative. The products are condensed by treatment with concentrated sulfuric acid.[143]

Chlorination of 2-methyl-α-naphthoyl chloride at 150 to 170°C. under the influence of arc lamp irradiation, and hydrolysis of the resulting product with water and calcium carbonate forms β-naphthylaldehyde-1-carboxylic acid.[144]

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[138] Berthoud, A., and Mosset, M., *J. chim phys.*, **33**, 272 (1936).

[139] Hamilton, C. S., and King, W. N., *J Am. Chem. Soc.*, **55**, 1689 (1933).

[140] Ellis, C., and McElroy, K. P., U. S. P. 914,251, March 2, 1909; *Chem. Abs.*, **3**, 1447 (1909).

[141] Davies, J. S. H , and Oxford, A. E., *J. Chem. Soc.*, 220 (**1931**).

[142] Kozak, J., and Pazdor, F., *Bull. Akad. Polonaise*, **A**, 477, 489 (1933); *Chem. Abs.*, **28**, 4114 (1934).

[143] British P. 427,327, April 23, 1935, to I. G Farbenind A-G.; *Chem. Abs*, **29**, 5866 (1935).

[144] Mayer, F., Schafer, W., and Rosenbach, J., *Arch. Pharm.*, **267**, 571 (1929); *Brit. Chem. Abs.*, **1928A**, 1294.

Tatum and Thomson[145] prepare α-halogenated anthraquinones by halogenating in the sun, or other actinic light, anthraquinone or its halogenated derivatives capable of further α-halogenation, in the presence or absence of halogen carriers, solvents or diluents. Thus anthraquinone is chlorinated in oleum in the presence of iodine under the action of sunlight, 1,4,5,8-tetrachloroanthraquinone being obtained. This, treated with phthalimide, and hydrolyzed to the tetra-amino-derivative, yields dyes which turn blue.

Phenanthrene can be brominated only by a light reaction.[146]

Terpenes. Cineole, in carbon tetrachloride solution, has been chlorinated in sunlight by Gandini,[147] who obtained a mono- and a di-chloro- derivative. Although light is indispensable for the formation of the mono-chloro- derivative, the reaction is slower and the yields are lower in ultraviolet light. In later work,[148] there was obtained from 100 gms. of cineole, 15 gms. of a mixture of 2-chlorocineole and 3-chlorocineole, 80 gms. of dichloroisomers, 25 gms. of a trichloro- derivative and 25 gms. of undistilled residue. A still higher percentage of chlorine led to more extensive chlorination and to products which could not be separated. Separation of the dichloroisomers yielded 2,3-dichlorocineole, an oil which slowly turns pale yellow on exposure to light.

Passage of chlorine into cumene containing 15 per cent acetic acid in sunlight affords *p*-chlorocumene and 1,3-dichloro-2-phenylpropane, the relative yields depending on the light intensity.[149]

Pseudocumene can be brominated by mixing with bromine and exposing to sunlight for about three hours.[150] The products formed depend upon the nature of the subsequent heating. If the exposed mixture is heated on a water-bath only the monobromide is obtained, but if it is heated to 170°C., a mixture of mono-, di- and tribromides results; the relative proportions depend upon the amount of bromine used. A mixture of 5-bromopseudocumene and bromine exposed to sunlight for three hours and heated for three hours gave di- and tri-nuclear substituted bromine derivatives in fairly good yields. In Bruylants's method for the preparation of trimethylene chlorobromide, allyl chloride is saturated with hydrobromic acid in sunlight. Strukov[151] finds the yield 95-97 per cent.

In direct sunlight in chloroform, camphane reacts immediately with chlorine with evolution of hydrogen chloride. The product yields bornyl chloride, which, treated in direct sunlight with chlorine in ice-cold carbon tetrachloride, yields a mixture of various halogenated derivatives difficult to separate Gandini[152] was able to obtain 2,3-dichlorocamphane, melting at 126-126.5°C., a trichloro- derivative, melting at 130-2°C., and other unidentified compounds.

Diphenosuccindan-9,12-dione in carbon tetrachloride may be brominated in the light of an arc lamp to the 10-bromo- compound.[153]

Light has no influence on the chlorination of lignin.[154] On the other hand, chlorination of wool is slower in diffused light than in direct light.[155]

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[145] Tatum, W. W., and Thomson, R. F., British P 364,141, Sept. 2, 1930; *Chem. Abs.*, **27**, 1640 (1933).

[146] Kharasch, M. S., White, P. C, and Mayo, F. R., *J. Org. Chem.*, **2**, 574 (1938).

[147] Gandani, A., *Gazz. chim. ital.*, **63**, 151 (1933); *Chem. Abs.*, **27**, 3707 (1933).

[148] Gandani, A., *Gazz. chim. ital.*, **64**, 118 (1934); *Chem. Abs.*, **28**, 4723 (1934).

[149] Varma, P. S., and Srinivasan, M. K., *J. Indian Chem. Soc.*, **13**, 189 (1936); *Chem. Abs*, **30**, 5949 (1936); see also Qvist, W., and Salo, A., *Acta Acad. Aboensis, Math. Phys.*, **8**, 4 (1934); *Chem. Abs*, **29**, 6884 (1935).

[150] Varma, P. S., and Sen-Gupta, D. N., *J. Indian Chem. Soc.*, **11**, 351 (1934), *Chem. Abs.*, **28**, 6119 (1934).

[151] Strukov, I., *Khim. Farm. Prom.*, **2**, 66 (1933); *Brit. Chem. Abs.*, **A**, 55 (1934).

[152] Gandini, A., *Gazz. chim. ital.*, **66**, 357 (1936); *Chem. Abs.*, **31**, 2595 (1937).

[153] Brand, K., Gabel, W., Ott, H., Müller, K, and Fleischbauer, R., *Ber.*, **69B**, 2504 (1936).

[154] Sarkar, P. B., *J. Indian Chem. Soc.*, **11**, 777 (1934); *Chem. Abs.*, **29**, 2514 (1935).

[155] Utaka, S., *Reports Imp. Ind. Research Inst. Osaka, Japan*, **15**, 11 (1935); *Chem. Abs.*, **29**, 2751 (1935).

Part III

Applications of Photochemistry to Industrial Products

Chapter 29

Reactions of Fatty Acids. The Preservation of Foods

In discussing the effects of light on the production of rancidity in foods, attention is first directed to the photochemistry of the fatty acids since these, when present as esters in fats and oils, are primarily responsible for the changes which occur.

It has been reported that acids with carbon chains longer than C_2, both saturated and unsaturated, become ketonic on exposure to light, atmospheric oxygen favoring the reaction.[1] The passage of air in the presence of tropical sunlight through solutions of potassium stearate, palmitate or oleate, according to Palit and Dhar,[2] is accompanied by oxidation, which increases with the intensity of the light. Zinc oxide is an effective photosensitizer.

The rate of oxygen consumption by undecenic acid, decenic acid, oleic acid and olive oil in light is greatly increased by the addition of very dilute solutions of chlorophyll or eosin as sensitizers, the former being ten times as effective as the latter. Hemin does not act as a sensitizer, at least for the oxidation of decenic and undecenic acids.[3] In the case of oleic acid, hydroxyoleic acid is formed. In general, there seemed to be no destruction of double bonds in these experiments.

Täufel and Seuss[4] found that the oxygen absorption, peroxide formation and epihydrinaldehyde formation in a highly purified sample of oleic acid was affected by light in the same manner as by the addition in darkness of such catalysts as ferrous, ferric or cupric chlorides. Custis[5] found the hydrogenation of oleic acid to be unaffected by ultraviolet radiations from an iron arc. A copper-egg white complex also catalyzes the oxidation of unsaturated fatty acids; this effect may be increased five to ten times by irradiation of the complex.[6]

Linoleic acid takes up oxygen and forms peroxides by a photochemical chain reaction.[7] The rate of peroxide formation is independent of the oxygen concentration and temperature and proportional to the concentration of acid and to the square root of the light intensity. As steps in the mechanism the following reactions were suggested (A is linoleic acid and M solvent):

$$\begin{aligned} &A + h\nu \longrightarrow A^* \\ &A^* + O_2 \longrightarrow AO_2^* \\ &AO_2^* + A \longrightarrow A^* + AO_2 \\ &AO_2^* + M \longrightarrow M^* + AO_2 \\ &M^* + A \longrightarrow M + A^*. \end{aligned}$$

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[1] Schmallfuss, H., Werner, H., and Gehrke, A., *Margarine Ind.*, **26**, 3, 87 (1933); *Brit. Chem. Abs.* **B**, 416 (1935).

[2] Palit, C. C., and Dhar, N. R., *J. Phys. Chem.*, **32**, 1263 (1928).

[3] Meyer, K., *J. Biol. Chem.*, **103**, 597 (1933). Certain porphyrins also inhibit the autoxidation of a mixture of linoleic and linolenic acids in sodium cholate solutions at pH 7.12. The inhibitors may be destroyed by ultraviolet irradiation. Hinsberg, K., and Ammon, R., *Z. physiol. Chem.*, **246**, 139 (1937).

[4] Täufel, K., and Seuss, A., *Fettchem. Umschau*, **41**, 107, 131 (1934), *Chem. Abs.*, **29**, 370 (1935).

[5] Custis, H. H., *J. Frank. Inst.*, **184**, 880 (1917).

[6] Kather, E., *Arch. exptl. Path. Pharmakol.*, **184**, 645 (1937); *Chem. Abs.*, **32**, 8448 (1938).

[7] Horio, M., *Mem. Coll. Eng. Kyoto Imp. Univ.*, **8**, No. 18, 26 (1934); *Chem. Abs.*, **28**, 5338 (1934); Horio, M., and Monden, S., *J. Soc. Chem. Ind. Japan*, **37**, 488B (1934); *Chem. Abs.*, **29**, 52 (1935); Horio, M., and Yamashita, S., *J. Soc. Chem. Ind. Japan*, **37**, 392, 416 (1934); *Chem. Abs.*, **28**, 7165 (1934).

Light rays shorter than 4000A are effective, ordinary sunlight having only a few suitable wave-lengths for oxidative action.

These observers also found that in the absence of oxygen the light of a mercury arc caused a bleaching of mixtures of aqueous solutions of linoleic acid with alcoholic solutions of eosin, Victoria Violet or erythrosin (but not Victoria Blue, which is non-fluorescent) more rapid than in darkness. The dye is reduced and the acid oxidized. The bleaching of the dye was less rapid when oxygen was bubbled through the solutions.

The rate of bromination of oleic, linoleic and linolenic acids is in inverse ratio to the number of double bonds they contain,[8] oleic acid acting the most and linolenic acid the least rapidly. Under the influence of ultraviolet light the bromination of both the so-called "pure" acids and the mixed fatty acids proceeds further than in darkness. This was held to indicate the presence of unsaturated isomers not revealed by the usual analytical methods.

As in the case of other unsaturated compounds, stereoisomeric transformations and polymerization reactions occur during irradiation. The former have been relatively little studied; the latter are discussed particularly in the following chapter.

Irradiation of "iodostarin" (di-iodide of tariric acid) in chloroform by sunlight, mercury-vapor light or Osram light, causes its dissociation into tariric acid and iodine.[9]

$$CH_3-(CH_2)_{10}\cdot CI=CI\cdot(CH_2)_4COOH \rightleftarrows CH_3-(CH_2)_{10}\cdot C\equiv C\cdot(CH_2)_4COOH+I_2$$

At room temperatures, the change is reversible and follows the law of mass action, but at higher temperatures there are deviations from this behavior. The equilibrium is independent of the strength of the light, but the rates of reaction are directly proportional to it. Since it was found that this decomposition is caused by the rays absorbed by the iodine, the photolysis must be regarded as sensitized by iodine.

Ultraviolet light promotes the formation of a diricinoleic acid by the condensation of the hydroxyl group of one molecule of ricinoleic acid with the carboxyl group of another.[10]

Lederer [11] investigated the effect of small concentrations of metals on the color of a two-to-one mixture of stearic and oleic acids in darkness, after eight hours in direct sunlight and after two hours of exposure at 40 cm. from an ultraviolet source. During neither of these exposures did manganese, aluminum, zinc or lead produce a color change. The presence of 0.04 per cent nickel led to a slight yellowing in sunlight but there was no color change after ultraviolet irradiation. Samples with 0.04 per cent copper exhibited distinct yellowing, and those containing iron showed considerable darkening, the effect being more pronounced in sunlight than in ultraviolet light. Samples lacking metallic adulteration were scarcely affected. It was concluded that the discoloration of fats after manufacture is primarily dependent upon the presence of traces of iron and copper.

Triglycerides are said to be hydrolyzed in the presence of water by the action of ultraviolet rays.[12]

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[8] Knauss, C. A., and Smull, J. G., *J. Am. Chem. Soc.*, **49**, 2808 (1927).

[9] Baur, E., *Helv. Chim. Acta*, **18**, 1149 (1935); *Chem. Abs.*, **30**, 28 (1936).

[10] Zlatarov, A., and Bieliavski, V., *Ann. univ. Sofia, Faculte phys.-math.*, **28**, No 2, 21 (1932); *Chem. Abs.*, **28**, 3054 (1934).

[11] Lederer, E. L., *Z. angew. Chem.*, **42**, 1033 (1929); *Seifensieder Ztg.*, **56**, 278 (1929); *Chem. Abs.*, **24**, 741 (1930).

[12] Tern, R., German P. 357,695; *J. Soc. Chem. Ind.*, **41**, 945A (1922).

DuNoüy[13] has called attention to a slight decrease in the surface tension of dilute sodium oleate solutions after three hours of exposure to light. Mahajan[14] attributes it to a chemical change which is most marked when ultraviolet light is used. The effect is at a maximum in soap solutions of 6.25×10^{-4} gm. per cc.[15]

OILS

Absorption and Fluorescence. The absorption of oils depends upon that of the acids they contain. In the case of cod-liver and other fish oils the well-defined absorption bands are due to sites of unsaturation. The highly absorbing acids obtained from them by saponification are apparently not, however, straight-chain compounds with conjugated double bonds since their absorption may be increased by prolonging the time of the saponification,[16] or by conducting it at elevated temperatures.[17] During this process cyclization probably occurs with the formation of hydroaromatic polycyclic products.

Considerable attention has been devoted to the absorption of fish-liver oils in connection with work on the distribution of vitamins A and D therein. (See Chapter 41.)

Of the vegetable oils studied, linseed oil shows the greatest absorption, according to Harvey,[18] who used an actinometric method which did not permit determination of the wave-length distribution of the absorption. Lewkowitsch[19] measured the absorption of thin films of whale, herring, olive, teaseed and linseed oils. Both the animal and vegetable oils gave curves of the same type, absorption gradually increasing toward the shorter wave-lengths. The feeble absorption bands superposed upon the more or less general absorption could not, however, be used for the purpose of determining individual oils in mixtures. Although Lewkowitsch found in some samples of olive oil indications of a band at 2750A, Lundé, Kringstad and Weedon[20] showed that the value of the extinction coefficient at this wave-length characterizes various samples of this oil. In virgin olive oil it was 10 to 22, in refined pressed oil 35-55 and in refined extracted oil 54-90. Two unrefined extracted oils, however, gave values of 80 and 120.[21]

The blue fluorescence follows the same trend. Cortese[22] has shown that the examination of the fluorescence of various samples of olive oils cannot distinguish natural (yellow) from refined oil (blue in general), since the addition of chlorophyll or carotene to refined oils imparts to them the fluorescence characteristic of expressed oils. It may be possible to remove this by animal charcoal. Fixed oils from damaged fruit behave like refined oils. Fixed oils from olives stored only two or three days also fluoresce blue-violet.[23]

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[13] DuNoüy, P. L., *Nature*, **131**, 689 (1933).

[14] Mahajan, L. D., *Z. Physik*, **98**, 388 (1935).

[15] Acidity developed in a saturated mineral oil when exposed to sunlight or ultraviolet light is believed by Woog, P., [*Compt. rend.*, **189**, 977 (1929)] to affect its spreading on solid surfaces.

[16] Dann, W. J., and Moore, T., *Biochem. J.*, **27**, 1166 (1933).

[17] Edisbury, J. R., Morton, R. A., and Lovern, J. A., *Biochem. J.*, **27**, 1451 (1933); **29**, 899 (1935).

[18] Harvey, E. H., *J. Am. Pharm. Assn.*, **19**, 1173 (1930); **20**, 643 (1931).

[19] Lewkowitsch, E., *J. Soc. Chem. Ind.*, **46**, 195T (1927).

[20] Lundé, G., Kringstad, H., and Weedon, H. W., *Angew. Chem.*, **46**, 796 (1933); Kringstad, H., *Angew. Chem.*, **49**, 423 (1936); Moore, T., *Biochem. J.*, **31**, 38 (1937).

[21] See also Rousseau, E., *Compt. rend. soc. biol.*, **96**, 611 (1927); *Chem. Abs.*, **21**, 1933 (1927).

[22] Cortese, D., *Industria chimica*, **9**, 1048 (1934); *Chem. Abs.*, **28**, 7044 (1934); Walter, C., *Olii minerali, olii e grassi, colori e vernici*, **15**, 149 (1935); *Chem. Abs.*, **31**, 6041 (1937); Fachini, S., and Martinenghi, G., *Olii minerali, olii e grassi, colori e vernici*, **17**, 54 (1937); *Chem. Abs.*, **32**, 3647 (1938).

[23] Ciusa, W., *Olii minerali, grassi e saponi, colori e vernici*, **18**, 33 (1938); *Chem. Abs.*, **32**, 8178 (1938).

Fluorescence colors excited by ultraviolet light have also been frequently suggested as aids in the identification of other fats and oils. Haitinger, Jorg and Reich [24] recorded the fluorescence colors of a number of oils and fats for use in the detection of adulterants in butter, cacao butter, lard, olive oil, etc. Butter is said [25] to give a golden yellow color, but margarine and synthetic fats appear grayish white. It is claimed that 20 per cent of foreign fat may easily be detected in this manner. Solid or molten lards [26] generally give a slight bluish fluorescence, but no definite conclusions may be drawn from its color as to the origin of the sample. Applied microscopically, the method may be used for distinguishing between shell and nib tissue in cocoa.[27] The brilliant white luminescence of cacao butter in the light of a quartz lamp is, according to Mauersberger,[28] due to traces of aluminum and calcium soaps formed while in contact with fullers' earth during bleaching. It is not characteristic of extracted butter because any pressed butter similarly treated with fullers' earth would give it.

Much attention has been devoted to the property possessed by seeds and oils of affecting a photographic plate as does light. Stutz, Nelson and Schmutz [29] believed it due to the evolution of hydrogen peroxide. The effect is greatly increased by exposure of the oils to light. Since only the unsaturated acids isolated from the oil, and not the saturated ones, are effective, the phenomenon appears to be associated with the drying of the oil. de Loureiro [30] attributed the effect to the evolution of ozone. The vapor from the oil must be brought in contact with the photographic plate.[31] Ried [32] believed that the effect in various fats parallels their ability to form vitamin D on irradiation. This has been much discussed, but at present is regarded as merely an incidental phenomenon. Irradiation does not affect the electrical conductivity of cod-liver oil.[33]

Photochemical Changes of Various Edible Oils. Wall [34] subjected cacao oil to the action of ultraviolet rays to destroy its objectionable taste and odor.

The bleaching of palm oil by light may be sensitized by the addition of various dyestuffs added to aqueous emulsions of the oil. Baur and Fabbricotti [35] estimated that the quantum yields when various dyes are employed is low, of the order of 10^{-3}. Exposure of olive oil to ultraviolet radiation for an hour has been found to cause an increase of more than 5 per cent in the acidity.[36] After exposure for about a week a comparatively rapid air-drying has been observed.[37] During exposure to ultraviolet, radium or x-rays, the dielectric constant, acid number and iodine number are the constants of olive oil which undergo the greatest change.[38]

Sun rays bleach layers of olive oil from 1 mm. to 1000 mm. in thickness, but the thicker the layer the slower the action.[39] For quick bleaching a maximum contact of oil, air and sunlight is needed. With oil flowing slowly down low steps, bleaching occurs in half the time. The bleaching does not completely destroy the fluorescence observed on exposure of the oil to Wood's light. Thirty days of exposure produced but little change in most of the constants, contrary to the observations of others on the effects of ultraviolet. Thus, the acidity was unchanged, the iodine number increased from 81.9 to 82.8, the refractive index changed from 1.46588 to 1.46625 and the saponification number decreased from 193.5 to 191.9. The density increased from 0.9170 to 0.9175.

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[24] Haitinger, M., Jorg, H., and Reich, V., *Z. angew. Chem.*, **41**, 815 (1928); Kaufmann, H. P., *Chem. Umschau Fette, Oele, Wachse, Harze,* **36**, 34 (1929); *Chem. Abs.*, **23**, 2051 (1929); Déribéré, M., *Mat. grasses,* **29**, 246, 279 (1937).

[25] Novacek, E., and Hokl, J., *Z. Fleisch. Milchhyg.,* **42**, 47 (1932); *Chem. Abs.*, **26**, 2881 (1932).

[26] Braunsdorf, K., *Z. Unters. Lebensm.*, **63**, 407 (1932); *Chem. Abs.*, **27**, 785 (1933).

[27] Wasicky, R., and Wimmer, C., *Z. Nahr. Genussm.*, **30**, 25 (1915).

[28] Mauersberger, E. A., *Chem. Ztg.*, **56**, 861 (1932).

[29] Stutz, G. F. A., Nelson, H. A., and Schmutz, F. C., *Ind. Eng. Chem.*, **17**, 1138 (1925).

[30] de Loureiro, A. J., *Compt. rend. soc. biol.*, **96**, 1321, 1324 (1927); *Chem. Abs.*, **21**, 2484 (1927).

[31] Hopwood, F. L., and Mayneord, W. V., *Nature,* **116**, 98 (1925).

[32] Ried, O., *Wien. klin. Woch,* **42**, 1105 (1929).

[33] Butler, L. W., and Woodrow, J. W., *Iowa State Coll. J. Sci.*, **11**, 333 (1937); *Chem. Abs.*, **32**, 4722 (1938).

[34] Wall, E. J., U. S. P. 1,386,476, Aug. 2, 1921; *Chem. Abs.*, **15**, 3913 (1921).

[35] Baur, E., and Fabbricotti, G. F., *Helv. Chim. Acta,* **18**, 7 (1935).

[36] Lesure, A., *J. pharm. chim.*, **7**, 575; *Chem. Abs.*, **5**, 963 (1911).

[37] Eibner, A., and Rasquin, H., *Chem. Umschau,* **33**, 29 (1926); *Chem. Abs.*, **20**, 2422 (1926).

[38] Kovalev, T. G., *Isvestiya Zentral. Nauch Issledovatelskog Inst. Pishchevoi Vkussovoi Prom., U.S.S.R.*, 3, (1931); *Chem. Abs.*, **26**, 5222 (1932).

Putland[40] observed a more rapid bleaching of vegetable oils in the light of Mazda lamps than in sunlight. Ultraviolet from a quartz mercury arc, however, darkened instead of bleaching both cottonseed and soybean oils. Crude cottonseed oil, one inch in depth, exposed in a tin tray at 27°C. to the mercury-vapor light, darkened from 35 yellow, 7.9 red (Lovibond scale) in eight hours to 35 yellow, 8.3 red. A bleached cottonseed oil changed in ten hours from 20 yellow, 2.1 red to 20 yellow, 3.0 orange.

In the laboratory of the senior author numerous experiments on the bleaching and polymerization of various oils by a Cooper-Hewitt quartz mercury arc have been made.[41] Samples of crude cottonseed oil, linseed oil, crude whale oil (No. 3) and a strongly fluorescent medium-body lubricating oil were exposed in shallow pans in three-sixteenth inch layers at about eleven inches from the lamp. After three hours the linseed oil had a very heavy film, the cottonseed and whale oils slight films but the lubricating oil was unaltered. After six hours the cottonseed oil had greatly increased in viscosity, the linseed and whale oil had commenced to gelatinize and the lubricating oil had become slightly darker. After 13½ hours, the cottonseed oil had gelatinized and was slightly bleached. The linseed oil had become a stiff jelly and its odor was diminished, but the color was apparently unchanged. The whale oil was considerably deodorized and slightly bleached. The lubricating oil had become somewhat darker, but the fluorescence had completely disappeared.

With exposures closer to the lamp, the whale oil gave a dark, amber-colored jelly with a very faint odor as compared with that of the original oil. Crude cottonseed oil also gave a stiff amber-colored jelly, which was considerably lighter than the original oil. The iodine value had fallen to 56. A highly refined cottonseed oil, however, gave a jelly which in color and consistency could scarcely be distinguished from that of the crude oil. The temperature during irradiation was about 110°C. The crude sample fumed slightly during the exposure to ultraviolet but the refined oil did not fume below 160°C. and then but slightly. Crude oil polymerizes and gelatinizes more rapidly than refined oil. Special experiments in sealed tubes showed that the thickening and polymerization occurs even in the absence of oxygen. In its presence, however, the solidification of unsaturated fatty oils appears to be due jointly to oxidation and polymerization. In one experiment made at a distance of but four inches from the source, a layer of cottonseed oil commenced to thicken immediately and at the end of fourteen minutes had completely solidified to a very thick jelly. A thicker layer (one and a half inches) at four inches from the lamp had become a solid, dark-colored jelly after 7¼ hours.

Castor oil after 10½ hours at three inches gave a product identical in appearance and odor with that obtained from cottonseed oil. Red oil (crude oleic acid) fumed slightly at 85°C and copiously at 110°C. A thin surface film appears to protect the under layer from further action until it is removed. When completely solidified it is hard without any tackiness, black and odorless. A highly refined corn oil gave in 14 hours at four inches a jelly of a very light yellow color, the change occurring very gradually. Immediately before the viscous mass commences to solidify, a large number of small bubbles usually appear below the surface and could be still observed even after the oil had become completely solid. In one case a mixture of equal parts of rosin and corn oil became extremely viscous and somewhat darkened after five hours. The carbonizing or discoloring action when very close to the rays was repeatedly noted. It may be partly due to a local superheating of the under layers of the oil.

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[39] Loew, G., *Olii minerali, olii grassi, colori vernici*, **12,** 89 (1932); *Chem. Abs.*, **26,** 6168 (1932).

[40] Putland, A. W., *Cotton Oil Press*, **7,** No. 7, 36 (1923).

[41] Ellis, Carleton, U. S. P. 1,089,359, March 3, 1914. Note also 1,179,414 and 1,180,025.

In one case ordinary cottonseed oil was mixed with 5 per cent of sulfur and exposed to the action of ultraviolet for three hours at 150°C. It remained liquid after treatment. On the other hand, an oil which had been exposed until it was practically at the gelatinization point and then treated with the same amount of sulfur, on further exposure yielded a black, rubber-like solid. Stamberger[42] stated that vulcanized triolein, which is soluble in acetone and benzene, after treatment with sunlight or ultraviolet light is converted into a solid mass of molecular weight over 7000, insoluble in these and other organic solvents and swelling in benzene. Applications to the making of artificial rubber latex for impregnating textiles and making varnishes have been suggested.[43] Ellis also observed that an oil which had been hydrogenated to a titer of 54°C., after an exposure of three hours to ultraviolet light remained unchanged in color, odor and viscosity.

Early attempts to use ultraviolet light in aiding the reaction of catalysts in the hydrogenation of oils do not seem to have been successful.[44]

It has been suggested that the presence of unhydrogenated oils in hydrogenated products may be qualitatively detected by taking advantage of the fact that the former are darkened and polymerized by ultraviolet light while the latter are unaffected. An exposure of several hours is required.[45]

Oxidation of Oils. Much attention has recently been devoted to studies of the oxidation of oils, particularly in regard to the light it throws upon the production of rancidity in foods on storage. Ultraviolet light has a powerful effect upon the susceptibility of cottonseed oil to oxidation.[46] This change depends, according to Greenbank and Holm,[47] upon reactions occurring prior to the period of active oxidation.

During the absorption of small quantities of oxygen oxides and peroxides are believed to be formed; these are sometimes termed "moloxides" of the unsaturated acids. They alter the oxidation-reduction potential in a manner which may be followed by the aid of methylene blue or other indicators. The reduction of this indicator when dissolved in an unsaturated oil is rapid in strong sunlight. By using a 100-watt Mazda lamp as a constant source, the rate of the change in the color of the indicator, followed photoelectrically, affords an indication of the susceptibility of the oil to undergo the changes which lead to rancidity. Horio[48] measured the rate of the reaction by determining the concentrations of peroxides formed during ultraviolet irradiation of oils while oxygen was bubbled through them. With linseed oil and linoleic acid the rates were independent of the time of irradiation, proportional to the concentration of acid or oil, independent of temperature and oxygen concentration and proportional to the square root of the light intensity. With olive oil, the rate decreased with time to a constant value. The rate-intensity curve for this oil showed a maximum. Certain substances (vanillin, jara-jara, *p*-nitraniline) accelerate the formation of peroxides in ultraviolet light but not in darkness in linseed oil.[49] Irradiation also accelerates the effects of manganese and lead abietates.

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[42] Stamberger, P., *Rec. trav. chim.*, **46**, 837 (1927); **47**, 973 (1928); Knight, B., and Stamberger, P., *J. Chem. Soc.*, 2794 (1928).

[43] Stamberger, P., and Auer, L., British P. 321,693, 1928; *Brit. Chem. Abs.* **B**, 652 (1930).

[44] Walter, H., *Seifensieder-Ztg.*, 442 (1913); cited by Ellis, C., "Hydrogenation of Organic Substances," 3rd ed., Van Nostrand, 1930; A mercury-sensitized process has been described by Karagunis, G., *Praktika Akad. Athenon*, **11**, 404 (1936); *Chem. Abs.*, **32**, 1580 (1938).

[45] Ellis, C., and Wells, A. A., *Chem. Engineer*, 221 (1918).

[46] Holm, G. E., Greenbank, G. R., and Deysher, E. F., *Ind. Eng. Chem.*, **19**, 156 (1927).

[47] Greenbank, G. R., and Holm, G. E., *Ind. Eng. Chem. Anal. Ed.*, **2**, 9 (1930).

[48] Horio, M., *Mem. Coll. Eng. Kyoto Imp. Univ.*, **8**, No. 1, 8 (1934); *Chem. Abs.*, **28**, 5339, 7165 (1934).

[49] Nakamura, M., *J. Soc. Chem. Ind. Japan*, **40**, 205B, (1937); *Chem. Abs.*, **31**, 6910 (1937).

The velocities of formation of peroxides during irradiation of tung and castor oils are less than those in linseed and tsubaki oils. The peroxides of all these oils are stable at low temperatures in ultraviolet rays.[50]

In the presence of inert gases, olive, peanut, sesame and colza oils were unaffected by ultraviolet light, but in the presence of oxygen there was an increase in density and a decrease in iodine number. The fluorescence changed from yellow to deep blue as the oils became decolorized.[51]

Olive, linseed and especially cod-liver oil gain in weight on exposure to air in the absence of light, possibly because of the absorption of oxygen. Preliminary irradiation of the oils by ultraviolet light for thirty hours enhances the rate during fifty days up to a limit beyond which it is decreased. In comparison with the others, cod-liver oil behaves as though it had already been irradiated. The formation of a compound with peroxide oxygen (detected by the liberation of iodine from potassium iodide acidified with acetic acid) shows a relation to the time of irradiation similar to that of the increase in weight.[52] Peroxides are formed in olive, mustard, cocoanut, Mahua, castor, sesame and linseed oils, butter and some carbohydrates when air is passed through them during exposure to sunlight. In the absence of air, peroxide formation is decreased. All the oil peroxides have the ability to oxidize slowly a solution of glucose at 40°C.[53] Fats are believed to form ketones by Schmallfuss, Werner and Gehrke [54] and saturated and unsaturated acids, glycerol, some esters, soap, beeswax, and cholesterol act similarly. The higher fatty acids are converted to lower acids, and glycerol yields volatile acids. When methyl laurate or glycerol were used, positive aldehyde tests could be obtained.[55]

Soybean oil is rapidly ketonized by light of wave-lengths under 4100A, several times as rapidly as methyl laurate which is appreciably affected only by rays shorter than 3300A.[56]

The prolonged action of ultraviolet light on lard destroys the material causing luminescence, raises the octoic acid value, and forms the substance responsible for the Kreis reaction of rancid fats.[57] The increase in octoic acid value may be due to pelargonic and azelaic acids formed by oxidation and fission of oleic acid. The substance responsible for luminescence may be a derivative of oleic acid, or of hydroxyoleic acid.

Weak artificial light accelerates the oxidation of beef fat and exposure to direct sunlight for a few minutes suffices to produce rancidity.[58] The reaction is autocatalytic, even brief exposure to light accelerating the subsequent oxidation. In beef fat, bleaching of the lipochrome occurs at a comparatively early stage of the oxidation process. At least during the early stages, oxidation in the presence of light has but little effect on the acidity of the fat. There is a distinct parallelism between the intensity of the Kreis reaction (a pink color test with phloroglucinol and hydrochloric acid in a benzene solution) and the active oxygen content of the fat (determined by the liberation of iodine from potassium iodide in acetic acid and chloroform). At low temperatures, however, the content of active oxygen increases more rapidly in a fat than does its ability to respond to the Kreis test. The reverse is true in bright sunlight. The different susceptibilities of various specimens of beef fat to oxidation depends on the chemical nature of the fat itself rather than upon other tissue constituents.

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[50] Nakamura, M., *J. Soc. Chem Ind Japan*, **40**, 229, 230 (1937); *Chem Abs.*, **31**, 7682 (1937).

[51] Francesconi, L., and Pinoncelli, L., *Ann. chim. applicata*, **24**, 242 (1934); *Chem. Abs.*, **28**, 6006 (1934).

[52] Delore, P., *Bull. soc. chim. biol.*, **11**, 74 (1929); *Compt. rend. soc biol.*, **99**, 807 (1928); *Chem. Abs.*, **23**, 724 (1929). See also Zinov'ev, A. A., and Drucker, S. V., *Masloboino Zhirovoe Delo*, **13**, No. 2, 6 (1937); *Chem. Abs*, **31**, 7682 (1937).

[53] Chacrabarti, S. N., and Dhar, N. R., *Indian J. Med. Research*, **17**, 430 (1929); *Chem. Abs.*, **24**, 2166 (1930).

[54] Schmallfuss, H., Werner, H., and Gehrke, A., *Fettchem Umschau*, **40**, 102 (1933); *Chem. Abs.*, **27**, 3838 (1933).

[55] Schmallfuss, H., Werner, H., and Gehrke, A., *Margarine-Ind.*, **27**, 79 (1934); *Brit. Chem. Abs.* **B**, 846 (1936); Lampitt, L. H., and Sylvester, N. D., *Biochem. J.*, **30**, 2237 (1936); *Chem. Abs.*, **31**, 3311 (1937). For a review, see Schmallfuss, H., Werner, H., and Gehrke, A., *Fette u.-Seifen.*, **43**, 211, 243 (1936).

[56] Werner, H., Gehrke, A., and Minkowski, R., *Margarine-Ind.*, **27**, 93 (1934); *Chem. Abs.*, **29**, 7103 (1935).

[57] Grossfeld, J., *Z. Unters. Lebensm.*, **55**, 376 (1928); *Brit. Chem. Abs*, **1928B**, 824.

[58] Lea, C. H., *Proc. Roy. Soc.*, **B108** 175 (1931).

Coe[59] suggests that under the photosensitizing action of chlorophyll, atomic hydrogen is liberated. This combines with molecular oxygen to form a loosely bound hydrogen peroxide, which unites with the unsaturated bond of the glyceride and produces the rancid compound. The presence of catalase, therefore, is related to its keeping qualities. Other photosensitizers are assumed to be present in animal fats.

Coe and Leclerc[60] observed that on keeping maize or cottonseed oils in darkness or in green light, high peroxide values may be attained without the usual indications of rancidity being observed. Similar samples exposed to full daylight became rancid in the same period. Those kept in the dark do so on subsequent exposure to light. Lampitt and Sylvester[61] found the Issoglio test useful in measuring the initial changes which take place. It is said to give a quantitative measure of these changes before the stage of positive Kreis tests has been reached. The taste of rancid butter fat produced by irradiation of ether and petroleum ether solutions in the presence and absence of air may be the resultant of two different changes, one due to structural changes in the glycerol portion and the other in the constituent to which the fat owes its original taste These changes may occur independently.[62] The distinction between rancid and tallow-like odors and tastes has been denied by Horowitz-Vlasova, Kachanova and Tkachev,[63] since both seem associated with the formation of various oxidation products such as hydroxystearic acid and epihydrinaldehyde. Lipolysis does not occur. Exposure of milk to sunlight catalyzes the oxidation of the fat.[64] Light also increases the peroxide number of butterfat.[65]

Effects of Colors of Protective Wrappers. Discrepancies are apparent in the reports on the effects of various colors on the deterioriation of oils. Greenbank and Holm,[66] Lea[67] and Coe[68] found green light to be least and orange light the most active. Blue light was thought to be somewhat more active than red light. Coe believed that oils protected by opaque or green wrappers showed no organoleptic rancidity after seven months, although they gave strong Kreis, peroxide and von Fellenberg tests. Davies, however, believed[69] that the preservative effect of Cellophane wrappers depends more upon the depth of color than upon the actual color. Deep green, blue, red or dark brown were equally effective in preventing the autoxidation of the fat of biscuit meal in exposures of forty hours to sunlight. Light green and heliotrope wrappers allowed some oxidation to occur and lightly tinted papers were entirely ineffective. Thin vegetable parchment did not allow active rays to pass, greaseproof paper allowed some to penetrate and transparent paper had no retarding action.

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[59] Coe, M. R., *Oil and Soap*, **15**, 230 (1938); *Chem. Abs.*, **32**, 8178 (1932).

[60] Coe, M. R., and Leclerc, J. A., *Ind. Eng. Chem.*, **26**, 245 (1934)

[61] Lampitt, L. H., and Sylvester, N. D., *Chim. et industrie, Special No.* **642** (March, 1931); *Chem Abs.*, **25**, 3737 (1931).

[62] For a general discussion of the chemistry of rancidity, see Russell, E. E., *Can. Chem. Met*, **20**, 346 (1931).

[63] Horowitz-Vlasova, L. M., Kachanova, E. E., and Tkachev, A D., *Z. Untersuch. Lebensm.*, **69**, 409; *Chem. Abs.*, **29**, 7679 (1935).

[64] Barkworth, H., *Dairy Inds*, **3**, 7 (1938); *Chem. Abs.*, **32**, 2230 (1938).

[65] Ritter, W., and Nussbaumer, T., *Schweiz. Milchztg.*, **64**, 59 (1938); *Chem. Abs.*, **32**, 7148 (1938).

[66] Greenbank, G. R., and Holm, G. E., *Ind. Eng. Chem.*, **25**, 167 (1933).

[67] Lea, C. H, *J. Soc. Chem. Ind.*, **52**, 146T (1933).

[68] Coe, M. R., *Siebel Tech. Rev.*, **9**, No. 2, 51 (1934); *Science*, **75**, 585 (1932); *Ind. Eng. Chem.*, **26**, 245 (1935); Coe, M. R., and Leclerc, J. A., *Cereal Chem.*, **9**, 519 (1932); *Chem. Abs.*, **26**, 6030 (1932); *Cereal Chem.*, **11**, 241 (1934); *Chem. Abs.*, **28**, 4925 (1934); *Oil and Soap*, **11**, 189 (1934); *Brit. Chem. Abs.*, **B**, 1018 (1934); *Oil and Soap*, **12**, 231 (1935); *Chem. Abs.*, **29**, 8371 (1935); *Oil and Soap*, **13**, 197 (1936); *Chem. Abs.*, **30**, 6587; *Oil and Soap*, **14**, 171 (1937); *Chem. Abs.*, **31**, 6494 (1937).

Morgan[70] attacked the conclusions of Greenbank and Holm and of Coe. He finds in studies on potato chips that yellow or red light has little ability to cause rancidity, the deleterious action being due chiefly to blue and ultraviolet light. He did not rely, as others had done, upon oxygen uptake or the peroxide test, but determined the time of exposure required for rancidity to become evident to odor and taste. The ratio of this to the time required for the same effects to be produced in the same lot of chips simultaneously exposed in uncolored transparent cellulose gave the rancidity-retarding value of the film. Both daylight and a General Electric S-2 sunlamp were used as sources. It was believed that the rancid odor and taste are due to aldehydes of high molecular weight formed by the oxidation of unsaturated linkages Tests of several hundred colored transparent cellulose wrappers indicated that their utility in retarding rancidity depended upon their transmission of blue and ultraviolet light. (See Figure 120.) Very small amounts of ultraviolet light had an extremely disproportionate effect. The results of the earlier observers were ascribed to their failure to take into account the passage of small amounts of ultraviolet light through some of their wrappers. The visible color tells nothing regarding the effectiveness of a wrapper. Morgan developed a yellow transparent sheeting of cellulose, known as Sylphrap RR Old Gold[71] (from Sylvania Corporation) of high visible transparency and complete ultraviolet opaqueness in the usual 0.001-inch thickness. The only visible light cut

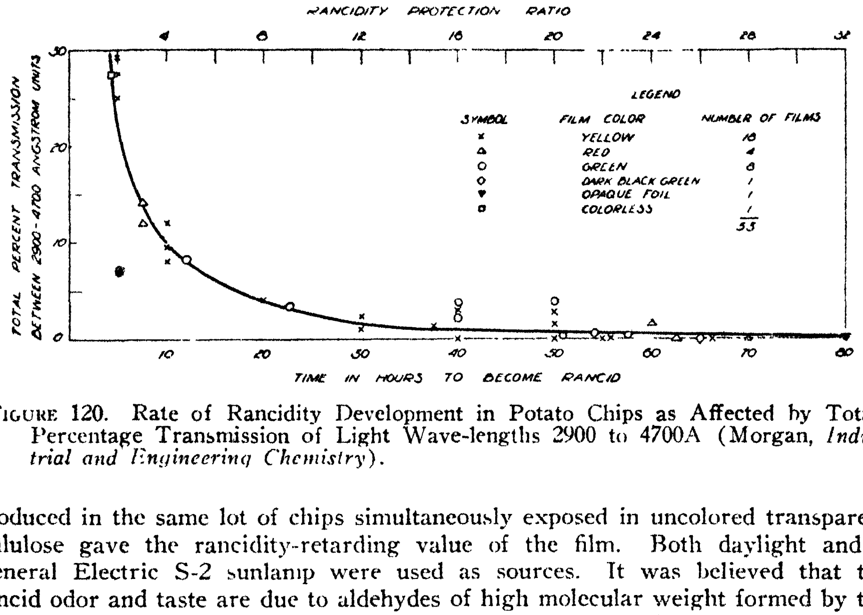

FIGURE 120. Rate of Rancidity Development in Potato Chips as Affected by Total Percentage Transmission of Light Wave-lengths 2900 to 4700A (Morgan, *Industrial and Engineering Chemistry*).

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[69] Davies, W. L., *J Soc. Chem. Ind*, 53, 148T (1934).

[70] Morgan, W. L., *Ind. Eng. Chem.*, 27, 1287 (1935).

[71] Morgan, W. L., *Modern Packaging*, May, 41, November, 84 (1934).

off is blue and practically all articles and foodstuffs wrapped in it appear in approximately normal color shades of red, brown, yellow or green. It is also recommended for protecting flavors of fruit juices, wines, brandies, flavoring extracts and perfumes as well as such drugs as phenol, calomel, quinine sulfate, and chloramine-T. It also retards the yellowing of paper and the sunlight aging of rubber.[72]

Wickmann [73] employs a deposit of particles of metal of atomic dimensions on the surface of gelatin or cellulose sheets in a granular non-flaking and non-cracking layer, giving the appearance of a continuous, lustrous coating.

As absorbing agents, Hunter proposes,[74] for incorporation in cellulosic wrapping paper, diaminobenzophenone and its homologs, derivatives of phenylhydrazine and aliphatic keto-acids, aminonaphthalenesulfonic or trisulfonic acids, *p*-hydroxyazobenzene, diphenylaminobenzene, resorcinolazobenzene or cresolbenzene. These absorb over the range 3200 to 4000A, and particularly 3500 to 3700A. Grant [75] employs on regenerated cellulose wrappers a coating composition of pyroxylin 3, amyl acetate or other solvent 5-25, a colorless absorber of ultraviolet light, such as esculin, 0.5-5.0, monoethyl ether of ethylene glycol for blending 3-10, a low-boiling solvent, ethyl acetate or acetone, 11-30, castor oil or other plasticizer, 2-5 parts, and a diluent such as benzene, toluene or naphtha.

In Germany, there is used for the protection of butter a parchment paper known as "Ultrament." This excludes practically all rays between 3540 and 2000A. Schlemmer [76] found one sample to show slight transmission at 2640A. It prevents tallowiness when used at 5°C.[77] but it cannot prevent that tallowiness which arises from the catalytic action of iron which may have been present in the wash water, a process in which light is not concerned. It does not affect bacterial growth on butter, so that rancidity may still develop from this cause.

Commercial parchment is opaque in the entire ultraviolet and infrared regions, according to Solechnik.[78] The transparency increases, however, after prolonged exposures to the weather, because of natural bleaching processes.

Parchment paper may be treated with various pyrene compounds such as sodium 3,5,8,10-pyrene tetrasulfonate, sodium 3-benzoyl-aminopyrene-*p*-disulfonate and the urea of sodium 4′-aminobenzoyl-3-aminopyrene disulfonate.[79] In other filters, one part of 3,5-dimethoxypyrene is dissolved in 99 parts of nitrocellulose lacquer and the solvent evaporated to leave a colorless film insoluble in water. A film of cellulose hydrate may also be passed through a bath containing 1 per cent of the urea of sodium 4′-aminobenzoyl-3-aminopyrene-disulfonate at 50°C. so that every part of the foil is covered by the liquid for one minute.

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[72] Morgan, W. L., U. S. P. 2,043,860, June 9, 1936; *Chem. Abs.*, **30**, 5442 (1936); British P. 453,438, Sept. 8, 1936; *Chem. Abs.*, **31**, 1113 (1937). Dyes are used incorporated in regenerated cellulose sheets Joseph, C., U. S. P. 2,038,114, April 21, 1936; *Chem. Abs.*, **30**, 3913 (1936); British P. 410,170, May 10, 1934, *Chem. Abs.*, **28**, 6312 (1934) uses as the absorbing agent a nonglucosidic coumarin derivative such as umbelliferone-acetic acid. Esculin, quinine, salol and anthracenes are also suggested All patents to Sylvania Industrial Corp.

[73] Wickmann, P. A., U. S. P. 2,039,372, May 5, 1936, to Sylvania Industrial Corp.; *Chem. Abs.*, **30**, 4232 (1936).

[74] Hunter, A. S., French P. 791,492, Dec. 11, 1935, to Soc. des usines chimiques Rhône-Poulenc; *Chem. Abs.*, **30**, 4232 (1936); Hunter, A S, U. S. P. 2,062,179, Nov 24, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, **31**, 789 (1937); Hunter, A. S., U. S. P. 2,129,131-2, Sept. 6, 1938, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, **32**, 8618 (1938).

[75] Grant, D. H., U. S. P. 2,058,786, to Stanco, Inc.; *Chem. Abs.*, **31**, 187 (1937).

[76] Schlemmer, F., *D. Molkerei-Ztg.*, **56**, 185 (1935); *Chem Abs.*, **29**, 2611 (1935); for a detailed discussion of factors affecting the deterioration of butter, see Jensen, J., and Ritter, W., *Lait*, **18**, 758 (1938); *Chem. Abs.*, **32**, 7147 (1938)

[77] Maier, Fr, *Deut. Molkerei-Ztg.*, **55**, 1477 (1934); *Chem. Abs.*, **29**, 2611 (1935).

[78] Solechnik, N. Y., *Bumazhnaya Prom*, **13**, No. 8, 24 (1934); *Chem. Abs*, **29**, 1244 (1935). See also Sommer, H., and Becker, J., *Zellstoff u. Papier*, **13**, 335 (1933); *Chem. Abs.*, **27**, 4669 (1933).

[79] British P. 457,708, Nov. 30, 1936, to I. G. Farbenind. A.-G.; French P. 804,582, Oct. 27, 1936; *Chem. Abs.*, **31**, 3602 (1937); see also Eggert, J., and Wendt, B., German P 640,908, Jan. 15, 1937, who use a urea derivative of sodium *p*-aminobenzoyl-*p*-phenylenediamine sulfate; *Chem. Abs.*, **31**, 5484 (1937).

Gerngross and Callo [80] use a dilute aqueous solution of pine-bark or quebracho extract in treating transparent papers or films of cellulose derivatives to make them impermeable to ultraviolet rays.

Paper milk bottles protect skim milk, whole milk or buttermilk against the action of sunlight in causing burnt flavors, but they do not protect whole milk or cream or homogenized whole milk and cream against tallowy flavors.[81] The burnt flavor predominates in low-fat and the tallowy flavor in high-fat products. Both commonly occur together in whole milk exposed to the sun. Homogenization of milk and cream accelerates the development of tallow flavor in sunlight, but retards that due to copper catalysis. The burnt flavor may have its source in the protein-free serum. It seems to be related to the fading of lactoflavin, which is the primary cause of the bleaching of milk in sunlight. This bleaching does not occur in paper bottles.

Ried [82] believed the stability of milk could be improved by keeping it in metal cans which had been previously irradiated by ultraviolet rays. He also proposed to pack butter and cheese in irradiated metal foil and believed the growth of yeast could be influenced by the use of irradiated metal vessels.

Soap bars with traces of iron or copper oxide darken in four days in diffused daylight and in a few hours in sunlight or ultraviolet light. [83] Sudden irregular after-darkening and rancidity of soap bars is traced to small quantities of rust or copper oxide from corroded parts of the equipment.

It has been claimed that a bactericidal substance may be obtained by irradiating a non-saponifiable portion of fatty material until it has an activity such that from 2 to 7 mg. per cc. of maize oil is fatal to yeast. Such a product may be mixed with inert oils or with lanolin to form medicinal preparations or may be added to cosmetics or shaving soaps.[84]

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[80] Gerngross, O., and Callo, A., British P. 459,335, Jan. 6, 1937; *Chem. Abs.*, **31**, 4021 (1937).

[81] Doan, F. J., and Myers, C. H., *Milk Dealer*, **26**, No. 1, 76 (1936); *Chem. Abs.*, **31**, 2304 (1937).

[82] Ried, O., Austrian P. 121,243, Sept. 15, 1930; *Chem. Abs.*, **25**, 2367 (1931).

[83] Wittka, F., *Seifensieder-Ztg.*, **54**, 740 (1927); *Chem. Abs.*, **22**, 177 (1928).

[84] British P. 423,354, Jan. 22, 1935, to Standard Brands; *Chem. Abs.*, **29**, 4526 (1935).

Chapter 30

Processes Involving the Polymerization of Oils, Paints and Varnishes

In discussing the bleaching of oils, it was impossible to avoid mention of the polymerization of unsaturated oils. The commercial processes which depend largely upon polymerizing and oxidizing effects are complex and are not as yet thoroughly understood. In addition, in unsaturated oils there are stereoisomeric transformations at double bonds. A separate treatment of these, and possibly other photochemical changes is scarcely possible as yet in a discussion of the mechanism of the drying of oils as influenced by light. Color changes also occur during drying.

Tung oil is the most suitable oil for studying the drying process because of its comparative freedom from mixed glycerides and because of its ability to yield purifiable products.[1] It was pointed out by Marcusson[2] that the white mass of melting point 32°C. formed in chinawood oil by ultraviolet light in the absence of oxygen cannot be a simple product of polymerization since the fatty acids liberated from it differ from those liberated from the original oil in melting at 71°C. They consist chiefly of β-eleostearic acid, an isomer of the α-form present in the original oil. Tung oil has 90 per cent of α-eleostearic (eleomargaric) acid. Accordingly, the formation of β-eleostearic acid is similar to the type of change discussed previously in connection with cinnamic acid. The formation of β-eleostearin causes the film of dried tung oil to lack durability. In addition to this process, there occurs also the formation of a small amount of an infusible polymerization product of β-eleostearin. This also is analogous to the type of change occurring in the cinnamic acid series. The change may be completed by 48 hours of irradiation, according to Böeseken and Ravenswaay.[3]

Manecke and Volbert noted[4] that eleostearic acid and its methyl ester have a deep absorption band at 2650 to 2750A. Dingwall and Thomson[5] went further in showing that two forms can be definitely identified by absorption curves. By studying the absorption spectrum of the α-form in alcoholic solution after various periods of mercury arc irradiation, it was found that during the first two minutes it tended to pass over into the β-form. Continued irradiation, however, caused profound changes. When a 15-per cent solution of the α-acid in 90-per cent alcohol was irradiated for two hours it was converted into an acid that had the same absorption spectrum (2500 to 2850A) as the acid obtained from the solid glyceride The absorption curves obtained by Manecke and Volbert for linoleic acid and its ester were different. They resembled those of oleic and crotonic acids with a slight increase in the intensity of absorption and a displacement of the characteristic weak absorption bands in the direction of longer wave-lengths. Absorption curves for acetic, elaidic, linoleic, eleostearic and stearoleic acids have recently been given by van der Hulst.[6] It will be recalled that in discussing the absorption of various unsaturated open-chain compounds, Smakula had shown the absorption to increase with the number of conjugated double bonds.

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[1] A critical review of the earlier work on the drying of oils and the nature of the "oxyn acids" was given by Eibner, A., and Munzert, H, *Chem Umschau*, **34,** 89, 101 (1927); *Brit. Chem. Abs.*, 417 (1927); *Chem. Abs.*, **21,** 2071 (1927) See also Morrel, R. S., *Chemistry and Industry*, **56,** 795 (1937)

[2] Marcusson, J., *Z. angew. Chem.*, **35,** 543 (1922); *Z. deut. Oel-Fett Ind.*, **43,** 162 (1923).

[3] Böeseken, J., and Ravenswaay, H. J., *Rec trav. chim.*, **44,** 241 (1925). Eibner, A., Merz, O., and Munzert, H., *Chem. Umschau*, **31,** 69 (1924); Nonaka, M, *J Chem. Ind. Japan*, **24,** 1272 (1921); Morrell, R. S., *J. Chem. Soc.*, **101,** 2082 (1912). Blom, A. V., attributes the change to rays of long wave-length, *Chem. Umschau, Fette Oele Wachse Harze*, **36,** 229 (1929); *Chem. Abs.*, **23,** 6336 (1929).

[4] Manecke, W., and Volbert, F., *Farben-Ztg.*, **32,** 2829, 2887 (1927); *Brit. Chem. Abs.*, **B,** 821 (1927).

[5] Dingwall, A., and Thomson, J. C., *J. Am. Chem. Soc.*, **56,** 899 (1934).

Eleostearic acid in carbon tetrachloride adds bromine rapidly in the light of a Uviol lamp until three double bonds are saturated.[7]

Eighteen grams of α-eleostearic acid in 180 gms. of petroleum ether in a freezing mixture was exposed by Bauer and Rohrback[8] in a quartz flask to ultraviolet light while adding bromine dropwise to the extent of six atoms per molecule. A white solid which separated after several hours, during which there was much evolution of hydrogen bromide, had the formula $C_{18}H_{30}O_2Br_6$. On debromination with zinc in alcohol, it gave β-eleostearic acid. An oily by-product of the hexabromide had a bromine content between that of penta- and hexa-bromide. When debrominated, it gave an oil with a bromine content between di- and tri-bromoeleostearic acid.[9] Of the three (conjugated) double bonds usually only two add bromine unless the solution is exposed to ultraviolet rays.[10]

Ellis found that chinawood oil at six inches from a mercury arc became so brittle after an hour that it could easily be pulverized to a white powder of iodine value 93. Linseed oil gave a resilient translucent jelly of practically the same color as the original oil.

Working with thin films of tung oil on glass slides, Eibner and Rossmann[11] found that exposure to sunlight or for ten minutes to a mercury arc causes a rapid formation of the crystalline β-eleostearin. Although at room temperatures, this is soluble in the unchanged oil, precipitation occurred if the film was kept at 0°C. The crystals could be observed microscopically under polarized light. This transformation is regarded as the first step in drying. In the absence of light, this isomerization did not occur. Oxygen is essential to the change of pure β-eleostearic acid to the amorphous condition, "filming"; this autoxidation is favored by light and by increase of temperature. The observation that during the conversion of this material into a film from 7 to 10 per cent of oxygen is absorbed invalidated the older theory that drying or film formation was a pure polymerization process. Examination of the fatty acids recovered from the product also showed that considerable oxidation had occurred. Polymerization probably also occurs so that film formation is a mixed process, "autoxypolymerization." Thus, if a tung oil containing β-eleostearin be exposed in a thin film, oxygen is primarily absorbed by the dissolved β-glyceride in the surface layers; the autoxypolymerization products are at first colloidally dispersed and then, by rapid transition to the gel condition, constitute a first disperse phase leading to film formation. Comparative experiments on the behavior of thin and thick films showed that the absorption of oxygen continues up to the drying point, and constitutes a principal reaction. Not all of the original α-eleostearin is transformed to the β-form before the autoxypolymerization occurs, for a tung oil kept in darkness for three to four weeks dried to a clear film. The greater part is directly autoxidized to a film.

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[6] van der Hulst, L. J. N., *Rec. trav. chim*, **54**, 639 (1935).

[7] Kaufmann, H. P., and Luten-Berg, K., *Ber.*, **62B**, 392 (1929). In methyl alcohol, two of the double bonds are saturated in darkness within an hour but the third only begins to react after fifteen hours. *Ber.*, **59B**, 1390 (1926).

[8] Bauer, K. H., and Rohrback, E., *Chem Umschau Fette, Waxe, Harze*, **35**, 53 (1928); *Chem. Abs.*, **22**, 2073 (1928).

[9] See also Kaufmann, H. P., *Ber.*, **59**, 1395 (1926); Böeseken, J., *Rec. trav. chim.*, **46**, 619 (1927).

[10] Kaufmann, H. P., and Baltes, J., *Ber*, **69B**, 2670 (1936); *Chem Abs*, **31**, 2032 (1937).

[11] Eibner, A., and Rossmann, E., *Chem Umschau*, **35**, 241 (1928); *Chem. Abs*, **23**, 291 (1929); *Brit. Chem. Abs.* **B**, 934 (1928). See also Merz, O., *Farbe und Lack*, **31**, 332, 343 (1926); *Chem. Abs*, **21**, 184 (1927).

Microscopic examination of films of chinawood oil on glass revealed a shrinkage in volume and the formation of fine cracks while the film was still moist, the cracks reaching through to the bottom.[12] This contraction coincides with the formation of β-eleostearin from the α-form. The next step in drying is the formation of folds at right angles to the cracks, increasing the volume and frequently pushing the cracks together again to form a double-lipped joint; this folding coincides with the absorption of oxygen by the α-eleostearin. Certain observations, however, stand in opposition to this simple theory. β-Eleostearin alone, when melted, will show contraction and crack formation and, as previously stated, the β-form also dries by a primary oxidation followed by polymerization. Light seems essential to the wrinkling, since clear, non-wrinkled films are obtained by drying the oil in darkness. In the light of the quartz lamp, this oil never dries clear; in sunlight at lower temperatures, there is wrinkling without cracking. α-Eleostearin does not appear to cause cracking at room temperature. It has also been observed in a black wood oil varnish that a network of fine cracks can form after the wrinkles have appeared, passing through the latter at all angles. Rossmann [13] states also that when ionized oxygen (produced by a flame, ultraviolet light or radioactive materials) was present during the drying of tung oil, wrinkles were formed, but that wrinkles did not form in the presence of ionized nitrogen or illuminating gas.

It has recently been suggested that a third form of eleostearic acid may exist. This is the punicic acid obtainable also from the seeds of the pomegranate. Ultraviolet light converts it into β-eleostearic acid.[14]

The properties of so-called "light-struck" tung oils were studied by Gardner and Parks.[15] Upon heating, the oils were quickly transformed into a clear liquid condition and could then be used for the production of varnishes as satisfactory as those made from oils which had not been "light-struck." Oils which had been exposed to sunlight for about six months could be brought back to a normal state by heating to about 60°C., although then their solidification points were very much lower than those of normal oils. Warming samples of the exposed oils with an equal volume of acetone gave clear transparent solutions, but on standing overnight these solutions gave heavy deposits of white crystals. Eibner would doubtless consider these as β-eleostearin.

Rossmann [16] exposed the α- and β-forms of eleostearic acid with and without solvents to sunlight and to the light of the quartz mercury arc. The products yellowed more or less, the iodine number decreased and the molecular weight increased. The decrease in iodine number determined by the usual methods did not indicate a loss of more than one double bond, but by the use of special methods it appeared to decrease by two in some cases. Various types of dimolecules may form through the loss of a double bond of each. It is also possible that the 1- and 6-carbon atoms of the three conjugated groups may join forming ring complexes. The amount of polymerization which occurs in 144 hours under the Hanau quartz lamp could be attained in a few minutes by heating at 300°C.

Lévy [17] has also described the microscopic wrinkling and folding of the frosty surface of tung oil films dried in air and light. The films formed by the much slower drying of the oil in darkness (six to eight weeks) are, if thin, nearly or completely free from frostiness. When dried in light, but in the dry atmosphere of a sulfuric acid desiccator, three weeks are required and only the thin films exhibit frostiness. Drying in a dry or moist vacuum requires about a year, but the surface is smooth. There is a loss of 1 to 3 per cent in weight. On opening the tubes there is an ethereal odor. Pressed oils do not solidify even when exposed for several months to sunlight or to an electric filament lamp. Oil obtained by extraction with petroleum ether solidifies in from a few days to a year in darkness, in a few days to a month in sunlight and in a few hours in the light of a mercury arc lamp. X-ray diffraction diagrams indicate that the solidified oil has a crystalline structure. In studies by means of the Siedentopf cardioid ultramicroscope, McCloskey and France[18] demonstrated a considerable increase in the number of colloidal particles and in the viscosity of tung and non-acidified linseed oils on irradiation.

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[12] Eibner, A., and Rossmann, E., *Chem. Umschau*, **35**, 281 (1928); *Chem. Abs.*, **23**, 1516 (1929).

[13] Rossmann, E., *Farben-Ztg.*, **38**, 1288 (1933); *Chem. Abs.*, **27**, 5557 (1933).

[14] Farmer, E. H., and van den Heuvel, F. A., *J. Chem. Soc.*, 1809 (**1936**).

[15] Gardner, H. A., and Parks, H. C., *Circular No.* **256**, *Paint Manufacturers Association*, December, 1925.

[16] Rossmann, E., *Fettchem. Umschau*, **40**, 96 (1933); *Chem. Abs.*, **27**, 5057 (1933).

[17] Lévy, P., *Recherches et inventions*, **14**, 340 (1933); *Chem. Abs.*, **28**, 3918 (1934).

Linseed Oil. The drying of linseed oil has been the subject of many investigations but cannot be said to be as well understood as is that of tung oil.[19] Kaufmann[20] gave data on the effects of light on the rate of the bromination of linseed oil in carbon tetrachloride and in methyl alcohol saturated with sodium bromide. The results, in Table 23 cited by Knauss and Smull,[21] are given as the equivalent of iodine absorbed by equal amounts of oil.

Table 23.—Bromination of Linseed Oil (Iodine No. 182)

	CCl_4		CH_3OH and NaBr	
Time	Dark	Sunlight	Dark	Sunlight
2 minutes	152.0	178.1	....	....
10 "	151.2	183.0	156.2	161.3
30 "	152.8	190.5	157.4	163.8
60 "	156.8	194.3	160.7	164.3
24 hours	183.0	239.5*	183.3	182.0
48 "	182.0	252.0	183.5	181.6

* No mention is made by Kaufmann as to whether any substitution had taken place to give these high values.

Knauss and Smull determined the rates of substitution and addition when bromine was kept with the fatty acids from poppyseed oil, soybean oil, linseed oil and perilla oil for one hour in darkness. They then observed increases in these values during subsequent exposure in quartz tubes to ultraviolet light during an hour. Similar observations were made upon oleic, linoleic and linolenic acids. The mixed fatty acids of the different oils all absorbed more bromine when irradiated than in darkness. This was held to indicate the presence of stereoisomers formed by light and not determinable by the usual methods of analysis. The possibility of a direct action of light upon the bromine does not seem to have been considered, probably because this effect would have been expected by visible rather than ultraviolet light.

Goldschmidt and Freudenberg[22] found that ultraviolet light failed to cause the polymerization of linolenic acid and its esters *in vacuo,* the process occurring only through oxygen bonds. Genthe[23] made early studies of the use of ultraviolet rays in the drying of linseed oil. It was exposed on filter paper to an atmosphere of oxygen in a quartz flask. During the first two hours of irradiation the absorption of oxygen was slight. In the third hour, it became very rapid, gradually diminishing in rate during subsequent hours. No formation of ozone was noted.

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[18] McCloskey, K. E., and France, W. G., *Ind. Eng. Chem.,* **27,** 160 (1935).

[19] For a review of early work, see *Farbe und Lack,* 629 (1926).

[20] Kaufmann, H. P., *Z. Untersuch. Lebensm.,* **51,** 3 (1926); *Ber.,* **59,** 1390 (1926).

[21] Knauss, C. A., and Smull, J. G., *J. Am. Chem. Soc.,* **49,** 2808 (1927).

[22] Goldschmidt, S., and Freudenberg, K., *Ber.,* **67B,** 1589 (1934).

[23] Genthe, A., *Z. angew. Chem.,* 2090 (1906).

In the laboratory of the senior author, samples of linseed oil were found to be considerably bleached by ultraviolet light[24] and in the case of the raw oil, practically no skin was formed over the top. With boiled oil, a film was formed in six hours if there was free access of air. In one case in which the oil was exposed in a thin layer over water, the oil became turbid and apparently a very stable emulsion was formed. In another case a sample of raw oil was exposed for seven hours in a closed chamber in an atmosphere of steam. The oil, which had been quite dark at the beginning, was bleached to a light straw color.[25]

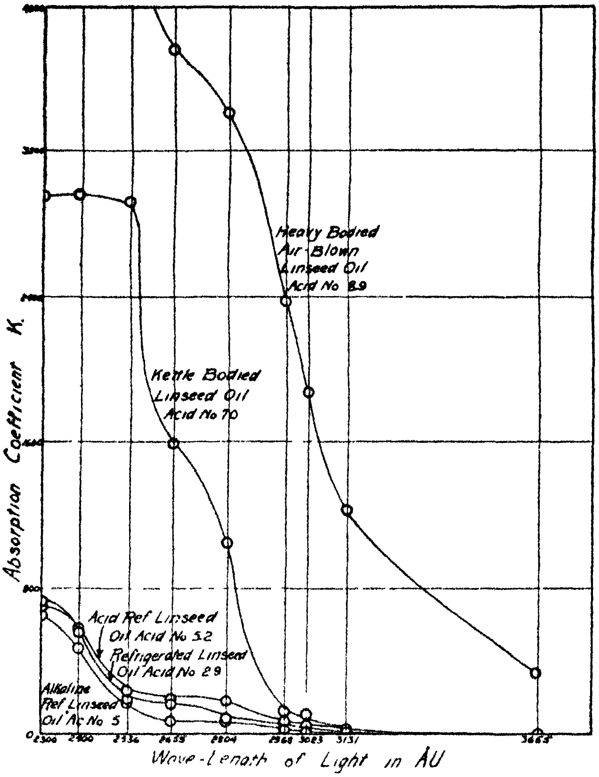

FIGURE 121. Absorption Shown by Several Samples of Commercial Linseed Oils (Stutz, *Industrial and Engineering Chemistry*).

Stutz[26] found the irradiation of raw linseed oil by ultraviolet in the presence of nitrogen to cause a marked decrease in the iodine number. This was confirmed by Knauss and Smull, who found that a sample of raw oil with iodine number of 180 showed only 148 after exposure for eighteen hours in dry carbon dioxide. But when this sample of oil was brominated in ultraviolet light for thirty minutes, the total bromine absorbed was equivalent to an iodine number of 190. In the first exposure of the raw oil in the presence of carbon dioxide, the ultraviolet rays caused a mutation of the stable isomers to labile forms. In the second exposure in which bromine was used, the action of the radiation stimulated the addition of halogen to the isomers formed in the first irradiation. It is known that labile isomers react very slowly with halogen and easily with oxygen. This too was found to be the case, for the oil from the first exposure (iodine number only 148) dried more rapidly than the raw, unexposed oil. It is apparent, therefore, that the ultraviolet rays must have simply stimulated the halogenation. It is unlikely that they could in thirty minutes have changed the labile form to the stable form.

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[24] See also Würth, K., *Farben Ztg.*, **33**, 1852 (1928); *Chem. Abs.*, **22**, 4261 (1928).
[25] Ellis, C., and Wells, A. A., *Chem. Eng.*, 116 (1918).
[26] Stutz, G. F. A., *Ind. Eng. Chem.*, **18**, 1238 (1926).

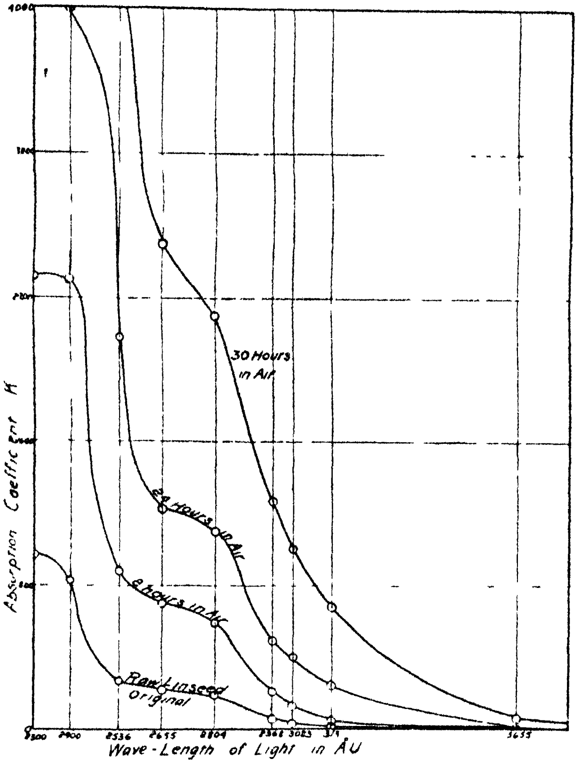

FIGURE 122. Change in Absorption Spectrum Shown by Raw Linseed Oil after Exposure to Ultraviolet Light in the Presence of Air (Stutz, *Industrial and Engineering Chemistry*).

An apparatus for oxidizing oils is described by Schofield.[27] The oil, such as linseed oil, is sprayed through a chamber illuminated by a high-tension electrical discharge. Purified and dried air is also supplied to the chamber, under pressure and at a temperature of about 250°C.

Gardner and Parks[28] found direct sunlight to accelerate the drying of a film of raw, unsiccatized linseed oil exposed to the air. There were no differences in the drying times in direct sunlight or in sunlight filtered through plain, ground, red, amber, blue or green glass. When, however, diffused daylight was employed the following times of drying were noted: Pure unfiltered light, 4 days; amber glass, 11 days; blue glass, 13 days; darkness, plain glass, ground glass, red glass or green glass, 14 days. The effect of heavily siccatizing the oil was to cause the films under all conditions, including exposure in darkness, to dry in six hours. Previous exposure of a film of raw unsiccatized linseed oil to the ultraviolet rays of an iron arc for thirty minutes produced a great acceleration in drying, which was shown to be independent of the heat resulting from the irradiation. When the ultraviolet rays were screened through red glass, the accelerating effect was lost.

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[27] Schofield, H., British P. 227,212, Oct. 16, 1923; *J. Soc. Chem. Ind.*, 180 (1925).

[28] Gardner, H. A., and Parks, H. C., *Circular* 172, *U. S. Paint Manuf. Assoc.*, March, 1923.

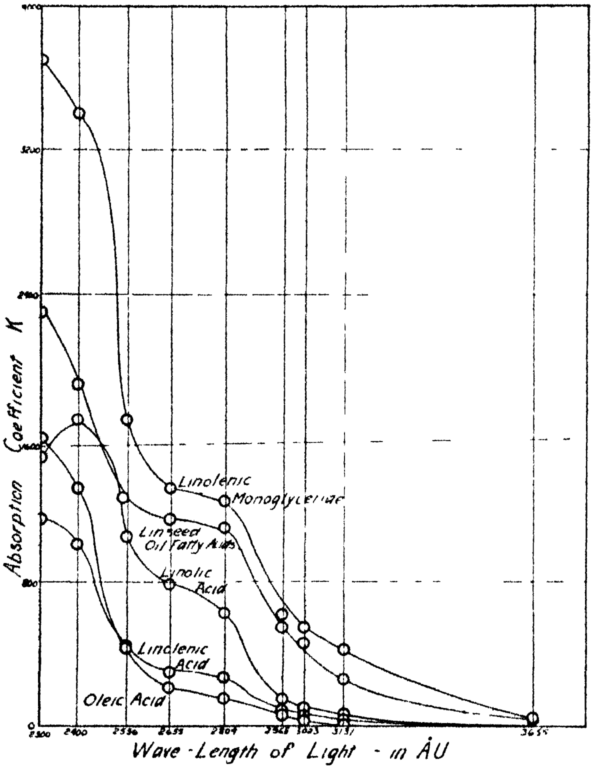

FIGURE 123. Absorption Shown by Acids Contained in Linseed Oil and Monoglyceride of Linolenic Acid (Stutz, *Industrial and Engineering Chemistry*).

Stutz [29] studied the influence of ultraviolet rays on a number of paint oils at 50°C., comparing their physical properties at various intervals. He also measured the absorption of the rays by these oils. In general, it increases with the molecular weight and body. The effect of exposure on wet oils is similar to the effect of heat and air-blowing. A boiled linseed oil absorbs the light almost completely at the surface. A raw oil, however, allows the light to penetrate a considerable distance. (Fig. 121 gives the absorption of several commercial samples.) Oils dried by exposure to ultraviolet light usually have a lesser absorption than those dried in diffused daylight. (See Fig. 122.) Practically all the oils studied, including linseed, tung, soybean, poppyseed and perilla oils, have high absorption of wave-lengths shorter than those at the limit of the sun's spectrum. Because the absorption is so nearly complete near the surface, changes occur there only and the properties of the underlying film are less affected. The radiations of sunlight, however, can penetrate more deeply. This difference deserves consideration in interpreting the results of accelerated weathering tests discussed in a subsequent section. The longer the oil is exposed the more it absorbs and, therefore, the greater the effect of light, which is cumulative. Bodying the oil seems merely to increase its content of absorbing materials. It cannot be due to an increase in acid content since the pure acids themselves have a lower absorption (see Fig. 123) than oil samples containing only 4 or 5 per cent of such acids. The similarity between the effects of ultraviolet on oil and the absorption changes during an air-blow of linseed oil (Fig. 124) make it probable that the decomposition or weathering of an oil film is simply a continuation of the drying of the film, the same reaction or reactions being involved in both.[80]

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[29] Stutz, G. F. A., *Ind. Eng. Chem.*, **18**, 1235 (1926); **19**, 897 (1927).

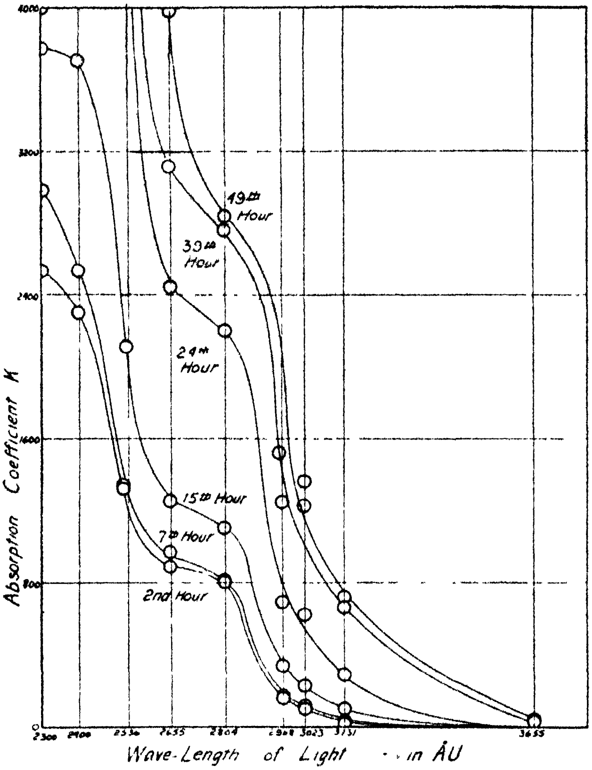

FIGURE 124. Absorption Shown by Several Samples of Linseed Oil Taken at Intervals during an Air-Blow (Commercial Scale) (Stutz, *Industrial and Engineering Chemistry*).

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[80] See also Becker, J., and Brückersteinkuhl, K., *Z. Kinderheilk.*, **43**, 566 (1927). For some observations on the effects of light on sunflower oil, see Kozin, N. I., and Fridlyanskaya, F. M., *Masloboino Zhirovoe Delo*, **12**, 529 (1936); *Chem. Abs.*, **31**, 5191 (1937).

Eibner and Munzert[81] noted that a linseed oil film in direct sunlight can lose in weight (after a first sharp increase due to oxidation) and may resoften, so that the standard test should be made in diffused daylight. Two oils treated with ultraviolet light were found to have gelatinized throughout their bodies after standing in darkness for several months, their acetyl numbers rising from the original 1.5 and 2.8 to 60.7 and 71.39, respectively, and their hexabromide numbers dropping from the original 51.5 to 13.8 and 9.6, respectively. Their gasoline-insoluble hydroxy-acids had increased from zero to 42.8. The normally dried films of linseed and poppyseed oils were thought to consist of glycerides of oxy-acids, although this could not be substantiated by chemical methods. The oxidized films are condensation products of the intermediately formed peroxides and are not true oxy-glycerides.

Marling[82] observed that linseed oil films without drier, or with a cobalt drier, on irradiation at 75 cm. from a mercury arc for a sixteen-hour period showed an increase in acid value and a decrease in iodine number. At a concentration of 0.015 per cent cobalt, the acid value reached 86 in this period. In an indoor aging test, 84 days were required for the oil to reach an acid value of 88.

It has recently been observed by Rose and Bolley that[83] unpigmented films of linseed oil, with or without drier, dry and harden when exposed under constant temperature and humidity to ultraviolet light, and then on continued exposure soften again. The percentage of the film insoluble in acetone reached a maximum at about the point of maximum hardness and decreased as the film softened again. The less saturated linseed oils gave dried films which softened less and were less soluble in acetone. Driers, lead or manganese, delayed and reduced the amount of after-softening. When pigmented with white lead, the films became progressively harder and less soluble with no after-softening. The iodine number, which was about the same for the soluble and insoluble portions of the film, decreased during exposure in all cases and was not related to the softening or solubility of the films.

Clark and Tschentke[84] made careful studies of the density changes during the drying of variously treated linseed oil films. For 32 hours of treatment by an intense sunlamp (equivalent to about six days of ordinary sunlight) the change in density varies from 2 to 4 per cent, depending on the drier. The highest change recorded was the unexpected one of 25.06 per cent for a raw oil film aged 226 days, though the density of this film had increased only 5.03 per cent in 68 days. This suggests that tests of linseed oil films must be run for a sufficiently long period. It also explains how paint films and patent leather may fail rather suddenly after a seemingly satisfactory period during several months. In the presence of driers this increase after periods of 248 days amounts to only 14 or 15 per cent.

Increases in density under ultraviolet light are smaller than in sunning, even though films may assume the same appearance and dryness. Where superposed films are involved, the mechanism of ultraviolet aging differs from that of sunning. After a film has been subjected to sunning or ultraviolet aging and is then placed in darkness, the increase in density continues at an increased rate. This is greatest after ultraviolet treatment. Although sunning requires hours, ultraviolet aging takes only minutes.

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[81] Eibner, A., and Munzert, H , *Chem. Umschau Fette, Oele, Waxe und Harze*, **34**, 89, 101 (1927); *Chem. Abs.*, **21**, 2071 (1927).

[82] Marling, P. E , *Ind. Eng Chem* , **21**, 594 (1929); see also Fukushima, I., Horio, M., and Miki, T., *J. Soc. Chem. Ind. Japan*, **35**, 142 (1932); *Chem. Abs* , **26**, 3939 (1932).

[83] Rose, C. H., and Bolley, D. S., *Ind Eng. Chem.*, **28**, 115 (1936).

[84] Clark, G. L., and Tschentke, H. L., *Ind. Eng. Chem.*, **21**, 621 (1929). A Mazda lamp source is used by Nicolson, D. G , and Holley, C. E., Jr., [*Ibid.*, **30**, 563 (1938)], who believe light destroys an inhibitor.

Auer[35] suggests treatment of linseed oil or castor oil with peroxides (*e.g.*, those of Mg, Zn, Ce or Na) and by heating at 250 to 300°C. under vacuum to obtain products which can be vulcanized and used as rubber substitutes. They may be employed also in the form of emulsions or as ingredients of varnishes, linoleum compositions, etc. In some cases, the products are further improved by exposure to ultraviolet rays or x-rays and by the use of such secondary reagents as formaldehyde, phenol, thiocarbanilide, benzidine, etc.

Experiments on the oxidation and polymerization of soybean oil were carried out by Taverne.[36] After ten days of exposure in air at room temperature, by Fahrion's method, the hydroxy-acids of three grams of oil on ten grams of cotton yarn were found to be 38.4 per cent. At 70° C., in the apparatus of Genthe[37] the oxidation was complete in thirty hours. By heating the irradiated oil in a beaker at 150° C., the molecular weight rose in ten days from 710 to 1730, indicating that polymerization accompanies oxidation. The oil became solid and contained 31.8 per cent hydroxy-acids and 63 per cent fatty acids soluble in petroleum ether, while the iodine number decreased to 64.8. Although Genthe had claimed that siccative oils can be bleached without oxidation, there was complete oxidation in 45 hours in Taverne's experiments. A lead (6.28 per cent) manganese (5.76 per cent) rosin compound was found to be the most active agent for hastening oxidation. On exposure to ultraviolet at 70°C., oxidation was complete with 5 per cent siccative oils in about ten hours.

Inaba, Kitagawa and Sato, and also Shinozaki and Sato,[38] exposed alcohol-extracted and benzine-extracted pressed soybean oils, both crude and refined, to ultraviolet light for sixty hours. After twenty hours, the alcohol-extracted and refined pressed oils were almost water-white, but it took thirty-five hours to decolorize crude pressed oil and benzine-extracted oil. Red colors were more easily bleached than yellow. The density, relative viscosity and refractive index increased with the time of exposure, sharply after fifty hours. For the first thirty hours the acid values remained constant, but after sixty hours they attained four to fifteen times their original values, reaching 4.5 to 5.5 no matter what they had been at the start. In the alcohol-extracted and refined pressed oils, the iodine numbers began to change after fifteen hours and in the benzine-extracted and crude pressed oils after thirty hours. After these periods, they decreased gradually. Fifty hours of exposure produced a substance soluble in petroleum ether; this amounted to 10 to 16 per cent after sixty hours. After 55 hours, the water-insoluble acids decreased by 2 to 5 per cent and the unsaponifiable matter increased 0.4 per cent. The oxygen content of the oils increased 4 to 5 per cent after ten hours. Both original and treated oils gave a weight increase of 6 to 7 per cent after 33 days. The ultraviolet absorption spectra also changed during the treatment, the oils becoming more opaque to the ultraviolet and less so to the visible rays.[39]

The carbon arc greatly accelerates the drying of various oils. Perilla oil set to touch in two hours.[40] Oils such as candlenut, poppyseed, menhaden and soybean set to touch in four to seven hours. The so-called semi-drying oils, corn, cottonseed and rubberseed, were found to dry in about 24 hours. Gardner[41] described apparatus suitable for drying newly painted walls.

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[35] Auer, L., U. S. P. 1,980,366, Nov. 13, 1935; *Chem. Abs.*, **29**, 254 (1935), see also French P. 652,796, Oct. 4, 1926; *Chem Abs.*, **23**, 3804 (1929). British P. 321,690, 1929.

[36] Taverne, N., *Z. angew. Chem.*, **28**, (I), 249 (1915).

[37] Genthe, A., German P. 223,419, Aug. 24, 1907; *J. Soc. Chem. Ind.*, 1168 (1910); *Chem. Abs.*, **4**, 3146 (1910). In this, the oil or fat at 70-90°C. is treated with rays from an immersed mercury arc while air is blown through the hollow arm of a stirrer. It is claimed that 1000 kilos of linseed oil can be bleached with an expenditure of 60 k.w. hours for current, 30 h.p. hours and 1500 cubic meters of compressed air for stirring.

[38] Inaba, T., Kitagawa, K., and Sato, M., and Shinozaki, Y., and Sato, M., *J. Soc. Chem. Ind. Japan*, **37**, 372, 374 (1934); *Chem. Abs.*, **28**, 7046 (1934).

[39] For further studies of the influence of air, oxygen, hydrogen peroxide, diffused daylight, direct sunlight and ultraviolet light on the physical properties and oxidation of soybean oil, see Horovitz-Vlasova, L. M., Katschanova, E. E., and Tkatschev, A. D., *Z. unters. Lebensm.*, **69**, 409 (1935).

In drying tests at the Institute of Paint and Varnish Research in Washington,[42] there is employed a metal drum revolving in thirty minutes and surrounding a low-pressure quartz mercury arc. In this apparatus perilla and linseed oils containing 0.02 per cent of cobalt became solid in 24 hours and tung oil in four hours. These products yield to hot acetone 20, 32 and 16 per cent, respectively, of unpolymerized products. The polymerized, sponge-like residues, after drying, were tested to determine the amount of a petroleum distillate they could absorb. That from perilla absorbed 70 per cent, from linseed oil 80 per cent and from tung oil 160 per cent of the mineral spirits before the surfaces of the particles appeared wet. These preliminary results indicated the possibility of producing these solid products from oil economically. Tung oil treated with 0.05 per cent sulfur produced a wax-like mass resembling a hydrogenated fat, which might be used in linoleum manufacture.

The yellowing of oxidized drying oils cannot be due to the presence or formation of ketohydroxy- compounds in the film, according to Elm and Standen,[43] since ketohydroxystearic acid is colorless, although diketostearic acid is yellow. From their appearances in filtered ultraviolet, the yellowing differs in tung and linseed oil films.[44]

Castor oil exposed to the sun in a thin layer solidifies fairly rapidly.[45] Polymerization of pilchard oil by ultraviolet rays shortens the induction period for its oxidation, and increases the rate of the process and the total amount of oxygen absorbed.[46]

The densities, refractive indices and saponification numbers of sunflower-seed oil samples are gradually increased by ultraviolet irradiation. The acidity increases comparatively little, the iodine number drops toward the end of a series of thirty irradiations (2 to 6 hours) at ten-day intervals. The acetyl number at first rises and then drops. The oil is bleached considerably.[47]

When fully extracted oil of the kernels of *Telfairia occidentalis*, which contains α-eleostearic acid, is exposed to diffused light for some weeks, very small yields of the β-isomer are formed. The yield is greatly increased by exposure to ultraviolet rays for some hours.[48]

In the oil of the pits of the Brazilian oiticica tree, the chief constituent is licanic acid (4-oxo-9,10,11,12,13,14-octadecatriene-1-carboxylic acid), which resembles eleostearic acid in being extraordinarily sensitive to light and air. The three double bonds make possible the existence of eight isomers, of which two are known. The fresh oil contains α-licanic acid, as glyceride which when illuminated in the presence of a trace of iodine, gives β-licanic acid.[49]

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[40] U. S. Bureau of Standards Notes, *J. Frank. Inst*, **206**, 694 (1928).

[41] Gardner, H. A., *Am. Paint Varnish Mfrs. Assoc. Circ.*, **335**, *July* (1928), 592; **330**, 482 (1928); *Chem. Abs.*, **22**, 3539 (1928)

[42] *Ind. Eng. Chem.*, **22**, 378 (1930).

[43] Elm, A. C., and Standen, G. W., *Ind. Eng. Chem.*, **24**, 1044 (1932).

[44] Eibner, A., *Paint Varnish Production Mfr.*, 14, 7, 10, 14, 12, 30, March, 1936; *Chem. Abs.*, **30**, 2779 (1936).

[45] Sunder, C., *Bull. soc. ind. Mulhouse*, **102**, 353 (1936); *Chem. Abs.*, **30**, 7348 (1936).

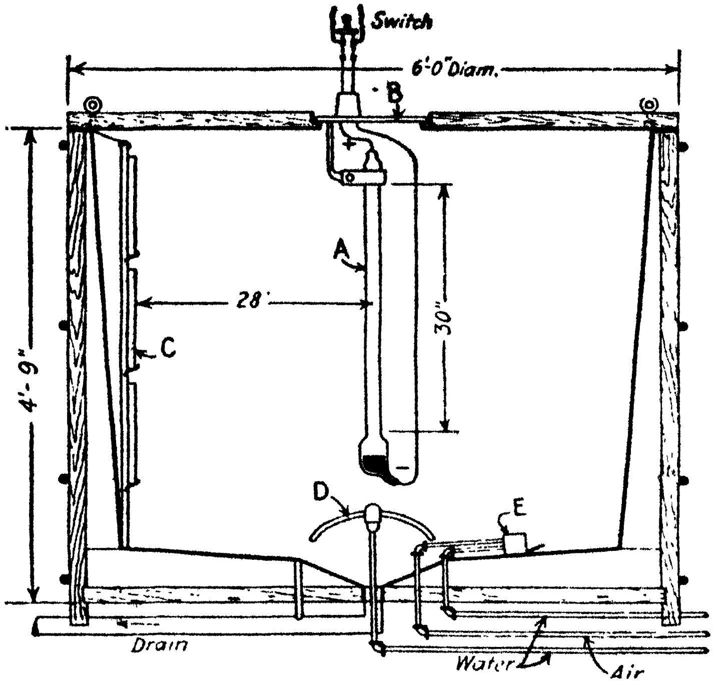
[46] Denstedt, O. F., and Brocklesby, H. N, *J. Biol. Board Can.*, **1**, No. 6, 487 (1936); *Chem. Abs.*, **30**, 2784 (1936).

[47] Kozin, N. I., and Fridlyanskaya, F. M., *Masloboino Zhirovoe Delo*, **12**, 529 (1936); *Chem. Abs.*, **31**, 5191 (1937).

[48] Farmer, E. H., and Paice, E. S., *J. Chem. Soc.*, 1630 (1935).

[49] Brown, W. B., and Farmer, E. H., *J. Chem. Soc.*, 1632 (1935).

Pigments. The effect of ultraviolet light on the darkening of lithopones has been discussed in Chapter 21. Some application has been made of ultraviolet-induced fluorescence methods in the determination[50] of the nature and quality of pigments, but many variable factors exist and careful control and considerable experience are necessary. The method is said to be valueless for estimating the pigment value of lithopones or zinc white, but natural and precipitated chalks may be distinguished by their appearances in ultraviolet light.[51] The presence of 25 per cent of zinc oxide in titanium white changes the violet fluorescence of the latter to a greenish yellow. The admixture of organic coloring matters in mineral pigments can frequently be detected by this method.



Courtesy Automotive Industries

FIGURE 125. Nelson Exposure Tank.

Kurotaki and Kobayashi[52] introduce 5 to 20 per cent of trivalent nitrogen organic compounds without acyl, alkyl or alkylene groups or their aldehyde condensation products in order to increase the light-fastness of pigments. Among the compounds used are α-naphthylamine, phenylenediamine, phenylazobenzene, phenylhydrazine and diazoaminobenzene.

The one salutary effect of light on paints is its bleaching action on yellowed surfaces. Whereas light of wave-length 3200A or less is required to produce pronounced deterioration of paints and darkening of lithopones, the beneficial bleaching action extends to much greater wave-lengths, in fact, up into the visible spectrum, according to some qualitative observations of Pfund.[53] On the other hand, in the case of nitrocellulose lacquers, the addition of any such plasticizers as dibutylphthalate, tricresyl phosphate, Sipalin AOM and Sipalin MOM increases the yellowing of the films on exposure to ultraviolet light, the effect being greatest with tricresyl phosphate, next with butylphthalate, next with Sipalin MOM and least with Sipalin AOM.[54]

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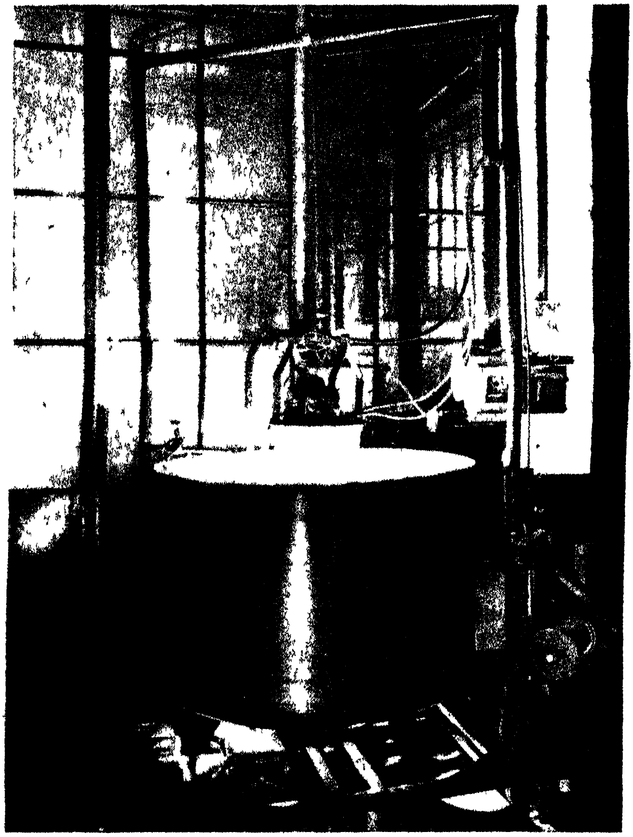
[50] Kufferath, A., *Farbe und Lack,* 473 (1935); Grant, J., *Oil and Colour Trades J.,* **85,** 1601 (1934); *Chem. Abs.,* **28,** 5997 (1934); *Paint Manuf.,* **7,** 340 (1937); Elm's, J., *Rev. gén. mat. plastiques,* **14,** 154 (1938); Bandel, G., *Angew. Chem.,* **51,** 570 (1938).

[51] Schoen, M. J., and Rinse, J., *Chem. Weekblad,* **26,** 321 (1929); *Brit. Chem. Abs.* **B,** 609 (1929).

[52] Kurotaki, S., and Kobayashi, C., Japanese P. 110,746, May 13, 1935; *Chem. Abs.,* **30,** 2411 (1936).



Courtesy National Carbon Co, Inc

FIGURE 126. Paint and Varnish Test Using Eveready C_6A Unit

Accelerated Weathering Tests.[55] Accelerated weathering tests for paint films have been devised by many, and usually involve the use of some ultraviolet light source to bring about in a short time the effects of sunlight over a prolonged period. It is readily apparent that there should be no reason to expect the short wave-length, highly active radiations to produce effects similar to those of the longer wave-lengths present in sunlight. Nevertheless, when their limitations are borne in mind, the use of ultraviolet tests may furnish in a short time comparative data which may be useful although they may not be in complete agreement with the results of prolonged fading tests.

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[53] Pfund, A. H, *Proc. Am Soc. Testing Materials*, **23**, *II*, 377 (1923)

[54] Wolff, H, and Rosen, B., *Farben Ztg*, **34**, 2564 (1929); *Chem. Abs*, **23**, 4835 (1929)

[55] A brief account of the historical development of accelerated paint tests has been given by Würth, K., *Farben Ztg*, **33**, 1470 (1928) For a general discussion of radiation and paint, see New, G F., *Paint Manuf*, **6**, 145-6; *Oil Colour Trades J.*, **89**, 787 (1936), and Masseille, H, *Peintures, pigments, vernis*, **8**, 1478 (1931).

Nelson[56] used a wooden exposure tank surrounded by an insulated air-space and lined with galvanized iron and containing a cylinder which revolves the test panels in a 24-hour cycle. Effects of sunlight, rain and mist were simulated by a quartz mercury arc, a revolving spray and a water-atomizer, respectively, together with a variable-speed electric fan to cool the arc and maintain a uniform temperature. (See Figure 125.) A more recent testing tank employs a carbon arc. (Figure 126.)

A cycle of exposure for 24 hours to the rays of the arc at a temperature of 50 to 60°C., followed by cooling and exposure to the water spray for another 24 hours at 5 to 10°C. was chosen as representing actual service conditions. Exposures were made at a distance of 28 inches from the source of the rays, investigation proving that the useful rays of destructive effect had a wave-length in the neighborhood of 3000A. On an average, comparable results were obtained in as many days in the apparatus as in months under service conditions. The following results were obtained on a series of paints, the figures referring to the number of days necessary for complete loss of gloss, and for initial chalking, respectively: 100 per cent lead-free zinc oxide, 14, 16; 100 per cent leaded (35 per cent) zinc oxide, 9, 12; 100 per cent light-resistant lithopone, 4, 6; 100 per cent basic lead carbonate, 3, 5; 100 per cent Titanox, 2, 4; a mixture of 40 per cent zinc oxide, 40 per cent lithopone, 20 per cent whiting, 9, 11. The effect of periodic saturation and maintenance of a saturated atmosphere during exposure is to accelerate both complete loss of gloss, and initial chalking by 50 per cent. Freezing of a saturated film materially promotes the formation of removable "chalk," most probably due to the formation of ice within the film. Neither flaking nor checking was reproduced in any of these tests. Cracking, rapidly followed by scaling and peeling, is produced by periodic exposures to temperatures considerably below freezing point, and is reproducible by exposures of equal alternate intervals to radiation, low temperature, and water-spray for a period of 100 days, equivalent to 14 to 15 months' exposure to the weather. Lack of adherence is a fault more strictly connected with the method of application of the paint, but can be brought about by exposure at 50 to 60°C. to the mercury arc. Of commercial paints intended for use as protective coatings for iron, both a 100 per cent red-lead paint and a mixture of 85 per cent ferric oxide with 15 per cent zinc oxide showed outstanding merit in maintaining gloss and inhibiting the formation of rust as compared with iron oxide paints containing various fillers, and a zinc oxide sublimed lead paint also containing a filler. Although a certain light-resistant lithopone maintained its whiteness over a period of three years on exterior exposure, the effect of the ultraviolet radiations was to discolor both this product and white lead in a short time.

Films exposed to ultraviolet rays increase in tensile strength and decrease in extensibility.[57] This effect is less pronounced with films containing zinc oxide, which is opaque to ultraviolet rays, than with films containing basic carbonate white lead, which is more transparent. The hardening and subsequent disintegration of the surface of a linseed-oil binder through reactions induced by ultraviolet radiation must be recognized as a fundamental cause for the failure of paints by chalking. This effect may be reproduced on pigments such as basic carbonate white lead by ultraviolet exposure alone without introducing any temperature or moisture variations.

Verification of the deteriorating effects of ultraviolet light came quickly from a number of sources. Thus, Wagner[58] claimed that the quartz mercury-vapor lamp gives the same final bleaching of 14 mineral pigments and 75 coal tar dyes as sunlight in one-fifth to one-thirtieth of the time, but noted that the type and quality of the vehicle influenced the results. The refractive index of the binding medium should be as near as possible to that of the pigment. In testing organic pigments or dyes, the least favorable medium for determining fastness to light is an aqueous glue wash, and the most favorable an oil or concentrated dextrin medium. The conversion factor of ultraviolet lamp hours into sun hours differs widely for different pigments.

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[56] Nelson, H. A., *Proc. Am. Soc. Testing Materials* **22**, II, 485 (1922).

[57] Nelson, H. A., and Rundle, G. W., *Proc. Am. Soc. Testing Materials*, **23**, II, 356 (1923); *New Jersey Zinc Co. Research Bull.*, March, 1930.

[58] Wagner, H., *Farben Ztg.*, **30**, 2991 (1925); *Chem. Abs.*, **19**, 3602 (1925); *Farben Ztg.*, **31**, 1023, 1073 (1926); *Z. Angew. Chem.*, **38**, 1191 (1935).

Discrepancies between the results of accelerated tests and outdoor exposures gradually became apparent. Gardner and Parks[59] believed that, regardless of whether the accelerated test wheel would determine how a coating will wear on exterior exposure, it is of great value in securing quick data in regard to the comparative aging of experimental coatings. Furthermore, as Dean pointed out,[60] the results of outdoor exposure tests are subject to factors difficult to control, such as climate, temperature range and the rate of its variation, rainfall, humidity, wind, abrasive dusts and various gaseous contaminants of the air. This accounts for the effort spent by many workers in developing the better controlled accelerated testing methods.

Nelson and Schmutz[61] balanced the weathering factors used in their tests to approximate at least roughly the order and relative magnitude of these factors as they appear in average outdoor weathering conditions. The weathering of a paint, varnish or lacquer surface may be considered a process of (1) rendering the film indistensible or (2) bringing about internal strains due to shrinkage, or both, and then of (3) revealing these weaknesses by the breaking up of the surface. The first of these usually involves oxidation, condensation and chemical decomposition. The second is usually due to temperature changes, which, in an indistensible film can be compensated for only by cracking and peeling.[62]

The apparatus of Nelson and Schmutz[63] consisted of a circular exposure tank four feet in diameter and sixteen inches in height with the destructive light source at the hub. A water spray, a silica gel dehydrator, and heating and cooling coils were included in an air-circulating system. Gas inlets and outlets for the introduction of oxygen and ozone when desired were provided. Refrigeration and water spray exposures were carried out in separate units, although it was also possible to use the water spray in the light exposure chamber. As a source, the flaming arc of the Atlas Electric Devices Co. Fade-Ometer was preferred to the quartz mercury arc since its spectrum more closely resembles that of the sun. It has approximately 34 per cent of its intensity below 4100A but none below 3100A. In comparative tests employing the mercury arc and the treated carbon arc in similar cycles, panels with three coats of a house paint lost 76 per cent in gloss and chalked badly with the mercury arc; they lost only 13 per cent in gloss and did not chalk with the carbon arc. The temperature should be 140°F. and certainly not higher than 160°F. Although light exposures accompanied by high humidity might be expected to show great destruction, most failures such as chalking and checking, were noted during light exposures at low humidity when given immediately after high humidity exposures. From stress-strain measurements on paint films, adsorbed water generally increases distensibility. Therefore, severer deteriorations may actually be taking place during a light exposure with high humidity but will not be so quickly revealed because of the additional distensibility induced by the adsorbed water. In a subsequent light exposure with low relative humidity, the previous weakening of the films shows up because the surface in the dry condition has a lower distensibility. This influence of humidity varies with the water resistance of the surface tested. In general, the humidity of the light exposure chamber should be made to conform to the ratio of high to low humidity conditions of the weather simulated. Checking, which was formerly difficult to reproduce in characteristic form, is promoted by the addition of oxygen up to 30 or even 100 per cent. In routine testing, 30 per cent is adopted. The temperature of the water spray is also of importance.

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[59] Gardner, H. A., and Parks, H. C., *Paint Mfrs. Assoc., U. S. Circular* 232, 248 (1925); *Chem. Abs.*, 19, 2560 (1925).

[60] Dean, H., *Chemicals* (Oct. 25, 7, 1926).

[61] Nelson, H. A., and Schmutz, F. C., *Ind. Eng. Chem.*, 18, 1222 (1926).

[62] Erosion is rarely considered. See Nelson, H. A., and Werthan, S., *Ind. Eng. Chem.*, 18, 965 (1926).

[63] Nelson, H. A., and Schmutz, F. C., *Proc. Am. Soc. Testing Materials*, 26, II, 563 (1926); Nelson, H. A., Schmutz, F. C., and Gamble, D. L., *Ibid.*, 26, II, 1 (1926).

One month in a suitable weathering cycle should approximate fourteen months of outdoor exposure, when a suitable addition of oxygen is made.

The Bureau of Standards employed [64] a flaming carbon arc. The regular test program is made up of exposure to ozonized air for three hours, rain for three hours, light for seventeen hours and inspection one hour. In addition, on three days each week, the panels are subjected to refrigeration at −23°C. for one hour, one-half hour being subtracted from the periods for exposure to ozone and rain. The order of exposures is varied on different days.

In a more recent description of the Bureau of Standards method, Hickson and Walker [65] state that the chamber for exposure to light and moisture consists of a rotating cylinder made of No. 16-gauge galvanized iron 76 cm. in diameter, 38 cm. high, open at both ends with the light-source suspended in the center. This size was selected to bring the light as near the panels as possible, at the same time avoiding too high temperatures. The cylinder has a capacity for sixty 7.5 × 15 cm. panels. These are placed in two tiers immediately opposite the light inside the cylinder, the panels thus being 38 cm. from the center of the light source. This gives a temperature of about 50 to 55°C. at the panels with the type of lamps used. Thirty slotted holders 7.5 cm. wide and about 35 cm. long for the panels are attached to the open surface of the open cylinder. A pan placed about 5 cm. below the bottom of the light cylinder contains water and serves to keep the temperature next to the panels down to about 52°C. as well as to humidify the air. To duplicate sunlight reasonably, an enclosed type carbon arc light operated at 220 volts d.c. and 13 amps. is employed. On each renewal of the carbons, the glass globe (opaque to wave-lengths less than 3200A) should be cleaned. To simulate a hot, humid climate, a fixed water spray is mounted in the tank in such a manner that it may function while the lights are operating. The light cylinders rotate slowly at three revolutions per hour. An ammonia coil about 27 × 47 × 40 cm. in an insulated chamber that can be cooled to −25°C. is used to chill the panels quickly. On removal from the light chamber, the test panels are placed in racks and the rack and samples are placed in the refrigerator, left there for one hour and then removed.[66]

In a method employed in Germany by Schulz [67] the paints are applied to iron plates and allowed to dry for at least three days, then matured for 24 hours at 80°C. The subsequent treatment consists of six repetitions of the following cycle: hanging in distilled water at 20°C., exposure to ultraviolet light while moist and again when dried, re-immersion in distilled water, enclosure in a damp atmosphere containing carbon dioxide, further exposure to ultraviolet light under damp conditions, and then at 50°C., enclosure in an atmosphere containing sulfur dioxide, exposure to damp air at 35 to 40°C., with interpolated periods at −5°C., and renewed action of ultraviolet rays. It was claimed that the results on zinc oxide-lithopone paints showed agreement with a two-year exposure to the atmosphere, in that the iron plates showed increasing rusting with the increase in proportion of lithopone to zinc oxide in the protecting paint.

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[64] *Tech News Bull., Bureau of Standards,* Sept. 4, 1927; Walker, P. H., *International Congress Testing Materials,* II, 603, 1927; *Chem. Abs.,* 23, 997 (1929).

[65] Hickson, E. F., and Walker, P. H., *Ind. Eng. Chem.,* 20, 591 (1928).

[66] Note also Davidson, J. G., and Reid, E. W., *Ind. Eng. Chem.,* 20, 199 (1928).

[67] Schulz, M., *Farben Ztg.,* 31, 2879 (1926); *Brit. Chem. Abs.,* B, 924 (1926); *Farben Ztg.,* 32, 2128 (1927).

In a rapid-testing apparatus described by Blom,[68] two parallel chains are mounted on tiers of cog-wheels two meters apart so as to carry between them fifty test sheets 10×20 cm. The chains travel at 20 cm. per minute and carry the sheets through three heating chambers and one freezing box. Sprays are fitted between the chambers, one of which can be filled with corrosive gases if desired. The strips are also submitted to both ultraviolet light and the light from a Sollux lamp. A typical time of treatment is only five days. Another German test machine described by Ritter[69] is claimed to give results in from 32 to 60 hours. An accelerated test has been patented by Digby, King and Kelvin, Bottomley and Baird, Ltd.,[70] and others have been described by Walter[71] and by Vila.[72]

Inconsistencies between the results obtained by the ultraviolet methods and outside exposures have led to renewed study of the effects of various light sources. Zeidler and Toldte[73] exposed eleven paints with various lead pigments on iron panels to radiations from the sun, an arc light, a mercury arc and a Nitra lamp, in some cases with a previous exposure to the action of hydrogen sulfide. The relative effects of the various sources on different paints were not uniform. In general, the mercury arc effected the greatest degree of fading of the discoloration produced by hydrogen sulfide.

Schmutz and Gamble[74] investigated the effects of six impregnated carbon arcs of known spectral energy distribution, the untreated carbon arc and the mercury arc on lithopones in nitrocellulose lacquers. Intensification of the infrared and visible ranges had but little influence on the results. One sample was unaffected by intensification between 3200 and 4200A. Two others were equally affected, although rays between 3000 and 3200A brought out a difference between them, and caused some effect on a third sample unaffected by the longer rays. With radiations below 3000A, the darkening was the same in the sample not affected at the longer wave-lengths and in only one of the two which had been equally affected by the longer rays. All samples showed up poorly. It is evident that specific wave-lengths exert specific effects on various samples of the same type of pigment. When wave-lengths shorter than 2500A are employed, the differences between samples become less marked.

The chief difficulty in the use of the carbon arc is due to the heat generated, elaborate cooling systems being required for its use in closed systems. Preliminary experiments indicated that the suitability of the mercury arc for this work could be increased by the employment of filters of Corning glasses.[75] Vitrified quartz burners were believed to have the advantage of not completely transmitting the far ultraviolet and of being more rugged than fused quartz.

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[68] Blom, A. V., *Chem. Fabr.*, 102 (1928); *Chem. Abs*, 22, 3789 (1928).

[69] Ritter, E., *Kali*, 23, 10, 26 (1929); *Chem. Abs.*, 23, 2048 (1929).

[70] Digby, W. P., King, F. A., and Kelvin, Bottomley and Baird, Ltd., British P. 429,792, June 6, 1935; *Chem. Abs.*, 29, 7100 (1935).

[71] Walter, P., *Bull. soc. encour. ind. natl.*, 134, 213 (1935); *Chem. Abs.*, 29, 5287 (1935).

[72] Vila, A., *Recherches et inventions*, 16, 26, 349 (1935); *Chem. Abs.*, 29, 6441 (1935).

[73] Zeidler, G., and Toldte, W., *Farben Ztg.*, 33, 1507, 2607 (1928); *Chem. Abs.*, 23, 3585 (1929); *Farben Ztg.*, 34, 1547 (1929); *Brit. Chem. Abs.*, B, 365 (1929).

[74] Schmutz, F. C., and Gamble, D. L., *Ind. Eng. Chem*, *Anal. Ed.*, 1, 83 (1929); see also Gardner, H. A., and Sward, G. G., *Am. Paint Varnish Mfrs. Assoc., Circular 358*, 64 1930; *Brit. Chem. Abs.*, B, 622 (1930); Nelson, H. A., *First Communications, New International Assoc. Testing Materials, Zurich*, 117 (1933).

[75] See also Becker, E., *Farben Ztg.*, 33, 2232 (1928); *Chem. Abs.*, 23, 1290 (1929).

Sward and Hart[76] compared the outdoor weathering of a number of coating materials with that produced by (1) a pair of 13-amp. enclosed carbon arcs, (2) a 50-amp. flaming carbon arc with Sunshine carbons, (3) a similar one with therapeutic C carbons and (4) a low-pressure mercury in quartz arc. Typical outdoor-type failures were obtained with the first and second sources, the latter being two to three times faster than the former. Failure by chalking predominated with the third and fourth even in materials which out-of-doors failed by checking. A combination of sources might be used to produce both checking and chalking. The operating costs are approximately 22, 21, 21 and 8.5-13 cents per hour for the four sources, exclusive of capital investment.

There has been much general discussion of the applicability of these accelerated methods. Grunder and Shepherd[77] believed them useful in comparing colors of the same basic type. The need for more refined methods for detecting failures has frequently been emphasized.[78]

The accelerated tests have the advantage of rapidity, constancy of results and ready adaptability to simulate peculiar exposure conditions.[79] Nettmann,[80] who is somewhat more critical of their value, attempted a theoretical discussion of the aging of paints on the basis of accumulation of potential energy in the films being responsible for changes in their inner structure. Nauroy[81] pointed out that no accelerated aging test could give the paint user an absolute or even a comparative measure of the value of a product submitted to him. Nevertheless, such tests can be of considerable value to the manufacturer for rapid control of the effects of variations in formulas. Williams[82] exposed panels of various yellow and green paints to ultraviolet light for 150 hours at 16 inches from the light. Warm air at 34°C. was continuously circulated around the panels. Failure was a darkening, probably the result of a reaction between paint and vehicle. Very pronounced chalking resulted but no great difference was apparent between panels of the same group. Gardner made some studies[83] of the water-soluble material produced by the action of weathering and ultraviolet light on various paints.

Sieplein[84] plotted the duration, intensity and fluctuational characteristics of outdoor ultraviolet radiation effective in exposure tests from astronomical and meteorological data for Miami and for a point representative of the eastern industrial region of the northern United States. Gardner[85] notes that paint films prepared indoors and stored in confined spaces often develop a mottled appearance when later exposed out of doors to the action of the sun.

The literature of the behavior of white pigments toward ultraviolet light has been reviewed by van Hoek.[86] Wagner[87] states that the inferiority of the chalk paints to those made from barium or calcium sulfates is not due to their impermeability to ultraviolet light, which is about equal to that of paints with barytes and other white bases, but appears to be due to the flocculated condition of the chalk particles in the prepared paint, to the fineness of the particles, to their soft texture, to the high oil content of the paint and to its great tendency to swell. The usual discoloration of titanium white paint is ascribed by Zhukova and Sovalova[88] to the instability of the titanium dioxide-linseed oil system because of poor wettability of the oxide by the oil. By using an oxide ignited at 800°C. instead of at 600°C., the discoloration in darkness is greatly retarded and that in ultraviolet light is practically eliminated. Soaps have a similar effect by forming pigment-enveloping aggregates which prompt the dispersion of the oxide in the medium.

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[76] Sward, G. G., and Hart, L. P., *Am. Paint Varnish Mfrs. Assoc. Circular 375,* 53 (1931); *Chem. Abs.,* **25**, 1105 (1931).

[77] Grunder, A., and Shepherd, R. S., *Paints, Oils Chem. Rev.,* **6**, No. 6, 8, 25 (1928); *Chem. Abs.,* **22**, 3538 (1928).

[78] Kempf, R., *Farben Ztg.,* **33**, 2359 (1928); *Brit. Chem. Abs.,* **B**, 578 (1928); Walker, P. H., and Hickson, E. F., *Ind. Eng. Chem.,* **20**, 591 (1928). Toldte, W., advocated the use of the Pulfrich step-photometer and the Ostwald color system for reporting the effect of light on paints, *Farben Ztg.,* **39**, 140 (1934).

[79] Eibner, A., *Farben Ztg.,* **34**, 322 (1928); *Brit Chem. Abs.* **B**, 63 (1929).

[80] Nettmann, P., *Farben Ztg.,* **34**, 2181 (1929); *Brit. Chem. Abs.,* **B**, 609 (1929); *Farbe und Lack,* 77, (1931); *Chem. Abs.,* **25**, 2009 (1931).

[81] Nauroy, A., *Chimie et industrie,* Special No. *683* (March, 1932); *Chem. Abs.,* **26**, 3681 (1932).

[82] Williams, J. J., *Am. Paint Varnish Mfrs. Assoc. Sci. Section, Circular 341,* 879 (1928); *Chem. Abs.,* **23**, 5334 (1929).

[83] Gardner, H. A., *Am. Paint Varnish Mfrs. Assoc. Circ. 313,* 368 (1927); "Physical and Chemical Examination of Paints, Varnishes and Lacquers," 4th ed., 183, 308, 1927.

[84] Sieplein, O. J., *Natl. Paint Varnish Lacquer Mfrs. Assoc., Circular No. 447,* 1, (1934); *Brit.. Chem. Abs.* **B**, 209 (1934).

[85] Gardner, H. A., *Natl. Paint Varnish Lacquer Mfrs. Assoc. Circular No. 455,* 66 (1934); *Chem. Abs.,* **28**, 3251 (1934). He describes an outdoor water-wheel test rack. *Natl. Paint Varnish Lacquer Assoc., Sci. Section, Circular 534,* 177 (1937); *Chem. Abs.,* **32**, 3639 (1938).

It is difficult to increase the fastness of chromes without adversely affecting the desirable properties of greening power or tinctorial strength and brightness of shade.[89]

To understand the susceptibility of various paint films to ultraviolet light, it is necessary to know something of the absorption of the harmful radiations by the pigments, since if they are so absorbed, there will be less energy to be absorbed by the oxidized oil film and less resulting deterioration of the film. At the same time, it is also desirable to know the relative abilities of various pigments, fillers and paint films themselves to reflect ultraviolet light. This is of some importance in the development of special paints for covering walls of rooms in which dual-purpose lighting is used.

Pfund[90] estimated the coefficients of diffused reflection from dry pigment surfaces by calculation from photographic records obtained by allowing the light reflected by a pigment surface from a small quartz mercury arc to enter the slit of a small concave grating spectrograph. When light falls on a thick layer of fine particles it penetrates a large number of particles before being returned, so that the reflection coefficients give roughly qualitative results for the opacities of the pigments examined. Zinc oxide became practically opaque near 3600A; basic carbonate white lead was by far the most transparent pigment examined. "Titanox," Timonox, lithopone, and sublimed white lead fell between these limits. Powdered sulfur is very opaque. Fused magnesia has constant reflecting power throughout the ultraviolet spectrum. In general, sulfur and zinc oxide are the most effective pigments in removing radiations harmful to the film. The inerts are the least effective. From studies of mixtures with a volume ratio of pigment to vehicle of 1:60 in films 0.065 mm. thickness, determinations of the decreased transmission due to pigment placed the transparencies of the pigments in the same relative positions as the determination of the diffused reflection coefficients. The transmission of the inert pigments is very high and is nearly non-selective.

Hallett[91] attacked the same problem in a somewhat different manner. The light from a quartz mercury lamp, after passing through a suitable glass filter to remove practically all the visible spectrum, passed through a quartz lens onto the painted surface from which it was either reflected or transmitted to sensitized paper.

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[86] van Hoek, C. T., *Farben Ztg.*, **34**, 833, 895, 954, 1006 (1929); *Brit. Chem. Abs.*, **B**, 180 (1929).

[87] Wagner, H., *Farben Ztg.*, 34, 2011 (1929); *Brit. Chem. Abs.*, B565 (1929).

[88] Zhukova, A., and Sovalova, A., *Za Lakokrasochnuyu Ind.*, No. 2, 11, 1934; *Chem. Abs.*, **29**, 3859 (1935).

[89] Barker, J., *Oil, Colour Trade J.*, **87**, 575 (1935); *Chem. Abs.*, **29**, 7675 (1935).

[90] Pfund, A. H., *Proc. Am. Soc. Testing Materials*, **23**, II, 369 (1923).

[91] Hallett, R. L., *Proc. Am. Soc. Testing Materials*, **23**, II, 379 (1923); *Chem. & Met. Eng.*, **29**, 64 (1923).

The paper was developed and the degree of blackening determined by measurements with a Howland color photometer, and calculated to the "Arturascale," in which the unexposed paper is taken as zero and the completely exposed paper as 100 per cent black. The values in per cent reflected, transmitted and absorbed by paints containing the following pigments (all in the same volume relation to the vehicle) are: Basic carbonate white lead, 42, 4, 54; zinc oxide, 0, 0, 100; basic sulfate white lead, 3, 0, 97; Titanox, 16, 0, 84; lithopone, 36, 1, 63; red lead, 1, 0, 99; iron oxide, 1, 0, 99; lamp black, 2, 0, 98. Further observations are due to Stutz.[92] New,[93] however, finds it impossible to predict from the transmission and reflection coefficients of pigments their effect on the durability of paint films exposed to ultraviolet radiation. In general, white paints are superior to aluminum paints in reflecting sunlight and in cooling power. Wagner and Pabst [94] find even thick films of white lead highly translucent to visible and ultraviolet light. Red lead is also transparent in thin but not in thicker layers. The addition of 50 per cent barite increases the translucency about 20 per cent. Finely dispersed hammerscale or lead reduction scale renders films opaque. Zinc white, so-called molybdate red lead, and iron oxide with zinc white or zinc chromate impart ultraviolet opacity.

The possibility exists that a pigment which absorbs energy may become excited thereby and may then pass over some of this energy of excitation to the film components. Goodeve [95] states that zinc and titanium oxides, which exhibit a steep fall in reflecting power at 3850 and 4000A, may serve as sources of photoactivation for the oxidation of oil vehicles or for the bleaching of adsorbed dyestuffs. He finds, however, that zinc oxide does not cause the oxidation of linseed oil, although titanium oxide does. The reduction of chalking by zinc oxide is a specific effect, attributed to internal filter action. Goodeve has also given the diffuse reflecting power of other materials such as lead carbonate, barium sulfate, magnesium carbonate and silica.

Luckiesh and Holladay [96] state that casein and nitrocellulose lacquer can be used as binders for ultraviolet reflecting paints, and that these should preferably contain a large proportion of magnesia, magnesium carbonate, alumina, or a mixture of these. Moderate amounts of silica, calcium carbonate, china clay and asbestine may be added without greatly reducing the reflecting power, which is about 5 to 65 per cent.

Lighting by luminous paints is proposed by Risler [97] A surface coated with a luminous paint containing a phosphorescent sulfide is rendered continuously luminous by subjecting it to the rays of the spectrum ranging from blue to ultraviolet. To obtain the rays, a vacuum tube activated by high-frequency currents and filled with gas, such as nitrogen, argon or air, is preferably used. In a modification of the process,[98] a vacuum tube with or without electrodes and filled with rarefied gas such as argon, nitrogen or air is coated internally or externally with a luminous paint containing a phosphorescent sulfide, or having the sulfide incorporated in the glass of the tube, whereby a continuous luminous effect is obtained. The sulfides may be mixed with a varnish and the luminous coating is preferably covered with an impermeable and fireproof coating comprising cellulose acetate, alcohol, triacetin, acetone and tetrachloroethane (see also Chapter 8).

[92] Stutz, G. F. A., *J. Frank. Inst.*, **200**, 87 (1925); **202**, 89 (1926); *Ind. Eng. Chem.*, **19**, 897 (1927).

[93] New, G. F., *J. Oil and Colour Chem. Assoc.*, **19**, 156 (1936); *Chem. Abs.*, **30**, 8652 (1936).

[94] Wagner, H., and Pabst, E., *Farben Ztg.*, **42**, 664, 691 (1937); *Chem. Abs.*, **31**, 8952 (1937); Kessler, *Farben Ztg.*, **43**, 39 (1938); *Chem. Abs.*, **32**, 4360 (1938).

[95] Goodeve, C. F., *Trans. Faraday Soc.*, **33**, 340 (1937).

[96] Luckiesh, M., and Holladay, L. L., *J. Frank. Inst.*, **212**, 787 (1931); *Chem. Abs.*, **26**, 5218 (1932).

[97] Risler, J., British P. 207,786, 1923.

[98] Risler, J., British P. 208,723, Dec. 20, 1923.

SYNTHETIC RESINS

Before discussing the applications of ultraviolet in the preparation and testing of varnishes, the relations of radiations to the artificial resins will be considered.[99] Some polymerization reactions employed in the preparation of vinyl resins have been mentioned in Chapter 23. Ramstetter[100] carried out the condensation of carbamide or its derivatives and formaldehyde under the influence of radiation of short wave-lengths, *e.g.*, from a quartz mercury lamp, in the presence or absence of condensing agents. The rays were applied during the whole or part of the reaction or during the concentration of the reaction solution or the hardening of the product. In one example, a solution of carbamide is treated at 75°C. with a mixture of 80 per cent formic acid and 30 per cent formaldehyde at 40°C. and heated for a quarter hour under reflux while being irradiated. Excess of formaldehyde is distilled off under reduced pressure at 40°C. till a syrup remains and the latter is poured into flat molds. On keeping, it finally forms transparent flexible flakes, the hardening process also being accelerated by exposure to ultraviolet light. Geisel[101] states that the hardening is accelerated and that a tendency to cloud or deposit is counteracted if the mass is subjected to the action of ultraviolet light. Shono[102] found a phenol-formaldehyde resin to be decolorized in proportion to the amount of the ultraviolet rays (3190-2585A) to which it was exposed. Most resins made from the condensation products of phenols and aldehydes present the difficulty of discoloration by light. The urea-formaldehyde resin has, however, been found relatively light-stable.[103]

A substitute for drying oils as a medium for paints, varnishes, and impregnating agents for fabrics, wood, etc., proposed by Röhm,[104] consists of a solution of polymerized acrylic acid ester in acetone, lower fatty acids or other solvents. When exposed to sunlight or ultraviolet light, the ester is transformed into a colorless, transparent, tough mass, soluble in solvents for oils.

The polymerization of the methacrylates is furthered by heat, light, oxygen and peroxides. These resins have extreme ultraviolet transmission and excellent light stability.[105] Wave-lengths shorter than 2200A decompose methyl-methacrylate vapor, but longer ones polymerize it to a white solid. Once started by light, the polymer continues to grow in the dark for several days. This growth is proportional to the area of the tube irradiated and the pressure of the vapor.[106]

Furfural resins have a good black color and completely absorb ultraviolet rays. By adding a suitable amount of Bakelite resin, they can supply a very fine ebonite-like insulating material or an effective coating varnish which protects ebonite from ultraviolet rays.[107]

In preparing lacquers in which a resin fast to sunlight or ultraviolet light is required, Moss and White[108] employ synthetic aniline (or other amine)-furfural resins, adding these to lacquers containing one or more derivatives of cellulose, such as cellulose nitrate, acetate, etc., and a volatile organic solvent, other natural or semi-synthetic resins, plasticizers, pigments or dyes. Phenol or ketone furfural resins also may be used.[109]

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[99] Fluorescence tests for the identification of resins have been tabulated by Wagner and Schirmer. Wagner, H., and Schirmer, H., *Farben Ztg.*, **43**, 131, 157 (1938); *Chem. Abs.*, **32**, 4361 (1938).

[100] Ramstetter, H., German P. 416,252, Jan. 31, 1923; *Brit. Chem. Abs.*, **B**, 99 (1926).

[101] Geisel, W., German P. 437,646 (1924); *Brit. Chem. Abs.*, **B**, 452 (1927).

[102] Shono, T., *J. Soc. Chem. Ind. Japan*, **30**, 143 (1927); see also *Chem. Abs.*, **20**, 2729 (1926).

[103] Ellis, C., *Chem. Met. Eng.*, 16, 1928; for the use of a sun lamp in testing the durability of color in brightly colored urea resins, see Houwink, R., *Trans. Inst. Plastics Ind.*, **5**, No. 9, 16; *Chem. Abs.*, **30**, 3905 (1936).

[104] Röhm, O., German P. 295,340, June 5, 1915; *J. Soc. Chem. Ind.*, 296 (**1917**).

[105] E. I. du Pont de Nemours & Co., *Ind. Eng. Chem.*, **28**, 1160 (1936); Barrett, H. J., and Strain, D. E., British P. 465,789, May 14, 1937; *Chem. Abs.*, **31**, 7444 (1937); Plauson, H., (Roehm and Haas Co.), U. S. P. 2,086,093, July 6, 1937; *Chem. Abs.*, **31**, 5811 (1937); Chalmers, W., U. S. P. 2,087,468-9, July 20, 1937; *Chem. Abs.*, **31**, 6378 (1937).

[106] Melville, H. W., *Proc. Roy. Soc.*, **A163**, 511 (1937); *Brit. Chem. Abs.*, **1938A**, 261.

[107] Ogawa, W., Hanyu, T., and Yanagihashi, T., *Researches Electrotech. Lab., Tokyo, No. 178*, 78 pp. (1926); *Chem. Abs.* **21**, 659 (1927).

Most of a series of synthetic and natural resins and gums studied by Gamble and Stutz[110] tended to decompose in ultraviolet light. This change was accompanied by a yellowing and an increase in the ultraviolet absorption coefficients. Ester gum was classified as being relatively opaque and also relatively stable to these radiations.

In general, the resinous materials are both more opaque and less sensitive to ultraviolet light than are the oleoresinous or nitrocellulose films. Incorporation of a resin therefore affords a certain degree of protection to such sensitive materials. The most desirable type of resin to use would be one which is both opaque and stable to these rays, but there are only a few such resin esters such as Congo, manila and rosin. It is also necessary to consider other factors, such as the physical and chemical properties of the resin and its resistance to weathering. Certain synthetic resins may have a chemical stabilizing action on nitrocellulose even though their own ultraviolet absorption characteristics may be undesirable. The phenol-formaldehyde, glycerol-phthalic anhydride and coumarone-indene types are fairly satisfactory. These all exhibit about the same high opacity, but differ in their sensitivity to the ultraviolet, the coumarone-indene group being the most readily decomposed. In general, the natural gums and resins are both less sensitive and more transparent than are the synthetic materials. Kauri gum was found to be the most stable of the natural resins measured. Vinyl acetate and vinyl chloride have high transparency but are considerably decomposed. A mixture of polymerized vinyl acetate and chloride is both more opaque and less sensitive than vinyl acetate alone.

With a view to obtaining photographic films more transparent than gelatin to the short ultraviolet rays, Dote and Shidei[111] measured the absorption of films from solutions of agar agar and of commercial viscose films. The films were more transparent than the corresponding solutions, which were themselves more transparent than gelatin especially in the extreme ultraviolet.

Minor[112] has employed ultraviolet for bleaching rosin. On the other hand, coumarone resin[113] is darkened on exposure to an ultraviolet lamp for three hours at a distance of a few inches.

The solubility of colored resinates submitted to the action of light has been investigated by des Bancels.[114] Colored resinates were prepared by treating resin with aqueous solutions of alkali hydroxides, adding a suitable coloring matter (safranine, rhodamine, etc.) and then precipitating with a salt of zinc or magnesium. These resinous substances, when dissolved in a volatile solvent, spread in a thin layer on glass plates, dried and exposed to a mercury-vapor lamp, became, at the end of a certain time, insoluble in such solvents as benzene, but soluble in methyl or ethyl alcohol.

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[108] Moss, W. H., and White, B. B., British P. 307,290, 1928, to British Celanese, Ltd.; *Chem. Abs.*, **23**, 5338 (1929).

[109] Moss, W. H., and White, B. B., British P. 307,291, 307,289, 1928, to British Celanese, Ltd.; *Brit. Chem. Abs.*, **B**, 469 (1930).

[110] Gamble, D. L., and Stutz, G. F. A., *Ind. Eng. Chem.*, **21**, 330 (1929).

[111] Dote, S., and Shidei, T., *Japan J. Physics*, **5**, 157 (1929); *Brit. Chem. Abs.*, **A**, 661 (1930).

[112] Minor, L. C., U. S. P. 939,733, Nov. 9, 1909; *Chem. Abs.*, **4**, 521 (1910).

[113] Ellis, C., and Rabinowitz, L., *J. Ind. Eng. Chem.*, **8**, 800 (1916).

[114] des Bancels, L., *Compt. rend.*, **155**, 280 (1912); *J. Chem. Soc.*, **102** (II), 882 (1912).

According to Chinchin,[115] the action of sun and electric rays on rosin causes the formation of a more stable form, insoluble in petroleum ether, having a different dielectric constant and resulting in a molecular agglomeration.[116]

The colloidal condition of stearates, palmitates and oleates of copper, aluminum, zinc, calcium and other water-insoluble soaps is affected adversely and their solubility is impaired by ultraviolet irradiation.[117]

VARNISHES AND LACQUERS

Wolff [118] believed the shrivelling observed to occur in varnishes dried in red light due to a slight retardation by the rays of the surface oxidation, and a greater retardation of polymerization in the inner layers. In light of shorter wave-lengths the processes were thought to proceed at nearly equal rates. Vollmann [119] believes the red rays cause an unequal distribution of heat which influences polymerization in the inner layers.

In the laboratory of the senior author, a large number of samples of varnishes of various grades have been exposed to ultraviolet rays. The behavior of varnishes varies greatly, depending on the composition. Some samples are bleached, others are darkened and still others are very little altered in color.

In the application and treatment of varnish, Clover [120] conveys the varnished articles through a chamber exposed to heat and to light rich in ultraviolet rays.

Ultraviolet accelerated weathering tests have been extensively used for varnishes, lacquers and enamels. Mougey [121] was unable to find a direct relationship between the results of these and of service tests when different types of materials were compared. In early tests made by Mougey on black baking fender enamel, panels failed on the test rack before they did under direct ultraviolet irradiation. When the panels were soaked in water over night and exposed to the ultraviolet during the day, they failed in a few days, but the results were of no value unless care was taken to remove surface water. Failure occurred in a few minutes at the areas where surface water lay on the panels. Finishing varnishes subjected to this test usually failed in one cycle, with no relation between the results of the test and the durability of the varnish. It was apparent that this test favored hard-drying finishes. A rotating wheel type of apparatus was used, half immersed in water and rotating at a rate of two revolutions per hour under the ultraviolet lamp. In this way the panels supported on the wheel were given time for drainage and evaporation of surface moisture and then exposed. A Duco nitrocellulose enamel which withstood exposure on the roof test rack for over two years failed in two days in this test. A finishing varnish with a life of three months on the roof test would stand two or three weeks on the wheel. Apparently, there was no connection between the results of the test and the life of finishing materials on the roof test rack. The results were better when the wheel was continuously rotated day and night and the lamp used only during the day.

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[115] Chinchin, I., *Bumashnaia Promyshlenost, No. 12* (1924); *Chem. Abs.*, **19**, 2273 (1925).

[116] For extinction coefficients of crude and bleached Japan wax, see Sakuma, I., and Momose, I., *J. Soc. Chem. Ind. Japan*, **38**, 218 (1935); *Chem. Abs.*, **29**, 5296 (1935). Crude wax showed a remarkable absorption at 6600A. Sunlight bleaching is facilitated by extraction of the pigment with alcohol. Sakuma, I., Momose, I., and Shomura, J., *J. Soc. Chem. Ind. Japan*, **40**, 48 (1937); *Chem. Abs.*, **31**, 6042 (1937); Sakuma, I., and Momose, I., *J. Soc. Chem. Ind. Japan*, **40**, 170 (1937); *Chem. Abs.*, **31**, 6495 (1937).

[117] Jones, H. I., *Chem. Met. Eng*, **28**, 489 (1923); *J. Soc. Chem. Ind.*, **42**, 410A (1923).

[118] Wolff, H., *Farben Ztg.*, **24**, 1119, 1389 (1919); *J. Chem. Soc.*, **115**, 915A; see, however, Ragg, M., *Farben Ztg.*, **24**, 1308 (1919).

[119] Vollmann, H., *Farben Ztg.*, **24**, 1427 (1919).

[120] Clover, G. R., U. S. P. 1,646,010, Oct. 18, 1927; *Brit. Chem. Abs.*, **B**, 916 (1927).

[121] Mougey, H. C., *Ind. Eng. Chem.*, **17**, 412 (1925); see also Jenkins, L. D., and Croll, P. R., *Ibid.*, **19**, 1356 (1927).

Wolff and Zeidler[122] prepared test films of the coating material on a colored gelatin film glued on paper strips. When dry, the film was placed with the coated side on a glass plate, and the gelatin removed with water at 50°C. It is then tested for tensile strength, elasticity and elongation. A kauri varnish film after exposure to the light of a quartz lamp showed an increased extension velocity.

Hansen[123] described a very simple and comparatively inexpensive test in which panels 2.5×13 cm. are exposed in a shallow pan under a source of ultraviolet light. By means of an intermittent siphoning apparatus, the panels are periodically covered with water and allowed to dry out. A cycle of one and one-half hours dry and one-half hour wet exposure was used, but the method when published had not yet been standardized with materials of known characteristics. Tognoni and Trolliet report favorable results with the Weather-Ometer.[124]

von Mühlendahl and Schulz[125] rotate a vertical wheel partly immersed in water, once in fifteen minutes. One day in this test is said to produce results closely paralleling one month of weathering.[126]

An embrittling test for predicting the durability of varnishes was devised by Wilson.[127] In it, varnish films on metal strips are exposed to a carbon arc or to Mazda lamps at a distance of 15 inches until they are so affected that they crack or whiten on bending double at 0 or 22°C. over a 3 mm. rod. The time of exposure to light required to produce this effect is taken as a measure of durability. Levy[128] found that this test, although valuable for classifying good and poor grade varnishes, would not rapidly distinguish grades of the newer types of synthetic resin coatings. An improvement by which the coatings are applied to surfaces of rubber sheeting that can be stretched instead of bent is suggested to make observation easier. Snitter[129] used a flexometer in which the test panel is gradually bent, the line at which bending is effected being observed under a magnifying glass. The angle at which fissuring of the varnish film occurs is noted. He did not find that artificial aging methods give results comparable to the effects of exposure to the weather.[130]

Nitrocellulose Lacquers. Particular attention has been devoted to the light-stability of the newer types of coatings. Stutz[131] made ultraviolet absorption studies of lacquer films, noting particularly the effects of the addition of plasticizers and gums. In general, the light penetrates some distance into the film before being completely absorbed. Similar data on films of acetylcellulose, both pure and plasticized with tritolyl phosphate and *p*-toluenesulfonanilide have been

[122] Wolff, H., and Zeidler, G., *Farben Ztg.*, 32, 2135, 2708 (1927); *Chem. Abs.*, 22, 1860 (1928).

[123] Hansen, H. V., *Ind. Eng. Chem.*, 20, 1384 (1928).

[124] Tognoni, C. A., and Trolliet, A. L., *Chimie & Industrie*, 38, 647 (1937); *Chem. Abs.*, 32, 3642 (1938).

[125] von Mühlendahl, E., and Schulz, H., *Z. angew. Chem.*, 40, 1185 (1927).

[126] For a description of a wheel developed by the Ditzler Co., see Denham, A. F., *Automotive Industries*, April 9, 1927.

[127] Wilson, J. H., *Bureau Standards J. Research*, 7, 73 (1931).

[128] Levy, S. A., *Am. Paint Varnish Mfrs. Assoc. Circular 410*, 146 (1932); *Chem. Abs.*, 26, 3939 (1932).

[129] Snitter, P., *Bull. inst. pins*, 223 (1933); *Chem. Abs.*, 28, 1554 (1934).

[130] See also Martin, R. C., *Metal Cleaning and Finishing*, 6, 561 (1934).

[131] Stutz, G. F. A., *Ind. Eng. Chem.*, 18, 1235 (1926).

given by Orlova.[132] Data are reported by Nakashima and Negishi [133] for various cellulose films as altered by swelling and softening agents.

The viscosity of nitrocellulose solutions decreases on exposure to light.[134] The colloidal changes occurring in nitrocellulose collodion with time and under the influence of ultraviolet light have been studied by Breguet [135] by fractional precipitation of the nitrocellulose by the method of Duclaux and Wollmann, using benzene instead of water to prevent precipitation of the camphor. The weight, viscosity and nitrogen content of the various fractions was determined. The results were interpreted in terms of the Duclaux theory of the constitution of reversible gels as follows: In a collodion the most complex nitrocellulose molecules have the greatest tendency to polymerize and swell, and in a nitrocellulose solution the solid phase is formed of the largest granules, the cells of which are filled with a dispersion of the finer granules of the solvent. The granules of collodion are in equilibrium with the solvent, and in time the cohesion forces of the molecules in the granules gradually diminish, and the granules are progressively depolymerized with resulting decrease in swelling, made evident by decreased viscosity. This aging does not proceed indefinitely but tends to a limit which depends on the concentration, temperature, and nature of the nitrocellulose collodion. Aging is accelerated by heat, light and mechanical treatment. The changes taking place in collodion with time are thus due to its changing from an emulsoid to a suspensoid. The general effects of ultraviolet light on celluloid or collodion are to lower the viscosities of all fractions and to decrease the total yield of high-viscosity nitrocellulose and correspondingly increase the yield of low-viscosity nitrocellulose.

Branchen and Prachel [136] proposed to make practical application of the ability of ultraviolet light to reduce the viscosity of an acetone solution of cellulose acetate in the presence of a fatty acid, preferably formic or acetic. In fifty hours a viscosity ranging from one-half to one-fifteenth that of the original value may be obtained.

During degradation by ultraviolet rays the tensile strength of cellulose acetate films with the same acetyl numbers varies as the viscosity. The stretch varies similarly but to a greater degree.[137] During this form of aging of a film base, there is associated with the depolymerization of the ester (shown by the decrease in viscosity) an increase in brittleness and a yellowing.[138]

When employed in layers in safety glass, nitrocellulose has been found to be light-sensitive, decomposing on prolonged exposure to light. Cellulose acetate promised better results as it is more stable, but it is still not ideal for the intermediate layer.[139]

It has been claimed that the instability toward light of nitrocellulose films depends on impurities introduced during preparation.[140] The most harmful impurities are ferrous salts, ferric salts being less so. Extraction of the nitrocellulose with hydrochloric acid can remove most of the iron salts. Decomposition products of cellulose, organic acids, aldehydes and sodium hypochlorite used for bleaching have no effect, but copper salts are also harmful. The photochemical stability is independent of the temperature of nitration and the thermal stability.

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[132] Orlova, O. V., *J. Tech. Physics, U.S.S.R.*, 4, 1170 (1934); *Chem. Abs.*, **29**, 8321 (1935).

[133] Nakashima, T., and Negishi, M., *J. Soc. Chem. Ind. Japan*, **39**, Suppl. binding, 102, 104 (1936); *Chem. Abs.*, **30**, 5407 (1936).

[134] McBain, J. W., Harvey, C. E., and Smith, L. E., *J. Phys. Chem.*, **30**, 312 (1926); *Chem. Abs.*, **20**, 1741 (1926).

[135] Breguet, A., *Rev. gen. colloides*, 3, 200, 230 (1925); *Chem. Abs.*, **19**, 3590 (1925). See also Rogovin, Z. A., and Glazman, S., *J. Gen Chem. (U.S.S.R.)*, **8**, 498 (1938); *Chem. Abs.*, **32**, 7260 (1938).

[136] Branchen, L. E., and Prachel, C. U., U. S. P. 1,658,368, Feb. 7, 1928, to Eastman Kodak Co.; *Chem. Abs.*, **22**, 1237 (1928).

[137] Grard, J., *Bull. soc. chim.*, **53**, 1308 (1933); *Chem. Abs.*, **28**, 4222 (1934).

[138] Kozlov, P. V., and Zueva, R. V., *Photo-Kino Chem. Ind. (U.S.S.R.)*, No. 5, 14, 1935; *Chem. Abs.*, **30**, 4107 (1936).

[139] Ellis, C., *Chem. Met. Eng.*, 16 (1928).

[140] Mindlin, S. S., Zel'dovich, P. Y., Kaplan, M. Y., Kuz'mina, L. I., and Remennikova, V. S., *Plasticheskie Massui*, No. 4, 4, 1934; *Chem. Abs.*, **29**, 3154 (1935).

Callahan[141] stated that a clear film of cellulose nitrate exposed to the ultraviolet rays of the sun's spectrum for only a few days becomes so brittle that it will not stand bending without cracking. The use of oils and plasticizers will extend this life but eventually failure will occur. However, if such a film is protected from the sun's rays by the use of opaque pigments, particularly when the film is applied to a rigid surface such as steel, almost indefinite resistance to sunlight will result. Scheiber[142] attributes the brittleness produced by light to the possibility of crystallization of the cellulose esters. In the absence of pigment, plasticizer and resin, ultraviolet light causes in nitrocellulose films a yellowing when wetted by 10-per cent sodium hydroxide, an increase in the wettability by water and ethyl acetate, an acid reaction and an unpleasant odor. The changes may be the result of saponification following the production of free organic acids.[143] Kraus[144] believes that the degree of yellowing in nitrocellulose lacquers depends on the nature and concentration of the plasticizer as well as on the exposure.[145]

It has been found[146] that the absolute intensity of yellowing of nitrocellulose films with 33.3 per cent tritolyl phosphate as plasticizer, when exposed to a mercury arc, was greater for 135μ films than for 15μ films. But when expressed as amount of yellowing per unit thickness, the change was greater in the thinner films. The amount of additional yellowing decreases for each added increment of time.

Kraus[147] finds that ultraviolet greatly impairs the plasticity imparted to nitrocellulose by butyl oleate or benzyl stearate. Palatinol AS and Palatinol L are superior. Irradiation caused strong yellowing with Toplast, somewhat less with benzyl stearate and very little with Palatinol AS, Palatinol L and butyl oleate.

Nishizawa[148] follows the rate of decomposition of nitrocellulose by light by determining nitrogen dioxide with α-naphthylamine. Kraus, however, did not believe the destruction of the film to be simply related to either the degree of denitration or to the loss of the solubility in acetone. Although the ability of the plasticizers to combine with the nitrogen decomposition products had an influence on the characteristics, direct relations could not be discerned.

Attempts have been made to increase the stability of nitrocellulose films to sunlight, *i.e.*, to decrease their chalking, by the introduction of pigments. McKim[149] prepared a clear cotton solution and in this ground a small amount of zinc oxide to determine whether a pigment opaque to ultraviolet light exerted a protective action. The reduction in distensibility produced by an ultraviolet exposure, which in the clear film caused a destruction of 100 per cent, was in this way reduced to but 60 per cent. The breaking strength of the clear film increased from 9 to 18 units and in the pigmented film from 30 to 36.

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[141] Callahan, M. J., *Chem. & Industry*, **47**, 34, 236T (1928).

[142] Scheiber, J., *Farbe und Lack*, 190 (1928); *Chem. Abs.*, **22**, 3054 (1928).

[143] Beutel, E., and Kutzelnigg, A., *Farbe und Lack*, 351 (1934); *Brit. Chem. Abs.*, **B**, 804 (1934); see also Gloor, W. E., *Ind. Eng. Chem.*, **23**, 980 (1931).

[144] Kraus, A., *Paint Varnish Production Mfr.*, **13**, 16, 18 (1935); *Chem. Abs.*, **30**, 307 (1936); *Farbe und Lack*, 545, 556 (1935); *Chem. Abs.*, **28**, 891 (1934).

[145] A general discussion of the aging of oil, gum, resin and cellulose derivatives under the influence of light and air and of the effects of pigments upon it has been given by Nauroy, A., *14 Congr. chim. ind. Paris* (Oct. 1934); *Chem. Abs*, **29**, 6443 (1935). Note also Rosenthal, L., and Schultze, G., *Farben-Chem.*, 53 (Feb., 1934); *Synthetic and Applied Finishes*, 65 (June, 1934).

[146] Communication III from the Untersuchungs-und Forschungs Laboratorium für Lacke und Farben, Berlin, *Farben-Ztg.*, **42**, 667 (1937); *Chem. Abs.*, **31**, 8960 (1937); Wolff, H., and Zeidler, G., *Paint Varnish Production Mfr.*, **17**, 7, 10 (Sept., 1938); *Chem. Abs.*, **32**, 7162 (1938).

[147] Kraus, A., *Farbe und Lack*, 269 (1938); *Chem. Abs.*, **32**, 8806 (1938).

[148] Nishizawa, Y., *J. Chem. Soc. Japan*, **50**, 258, 327, 391 (1929); *Chem. Abs*, **25**, 5627 (1931).

[149] McKim, W. A., *Ind. Eng. Chem.*, **18**, 1239 (1926); de Waele, A., *J. Soc. Dyers Colourists*, **43**, 42 (1927).

For the protection of automobile finishes, Denham[150] found a fairly large amount of pigment necessary. Although opaque colors in general stood up better than those of lower opacity, some, notably the Para toners, did not furnish as much protection. Although more opaque than madder lakes, they made up into less durable lacquers. White pigments (titanium, lithopone, zinc oxide) are very durable but zinc sulfide is undesirable, since it turns brown on exposure. Ultramarine lacks durability, since it does not provide protection against actinic rays. Of true lake colors, alizarin pigments produce the most durable so-called lake colors in pyroxylin lacquers. Since they have poor covering qualities, they must be strengthened with other materials which detract from durability.

In discussing accelerated weathering of lacquer enamels, Nelson[151] noted that it is possible to produce such failures as hair-line checking by increasing the oxygen content of the air in the light-exposure chamber and by including periodic exposure to humid air containing sulfur dioxide and carbon dioxide. He believed the relative ratings of a series of nitrocellulose lacquers in this test agreed reasonably well with outdoor exposure ratings.

Pigmented enamels made with cottons of higher viscosity showed greater durability and greater tensile strength and distensibility than those made with 0.5-second cotton. This may be due to the longer fibers used in the production of the cottons of higher viscosity, or to the freedom from suspended matter usually present in the solutions of the latter. Greater durability resulted from a ternary mixture containing 50 per cent of 0.5-second cotton, 24 per cent of 4-second cotton and 26 per cent of leather dope. The last by itself showed the poorest durability of all the cottons tested.

In weathering, light-colored enamels containing 19.5 per cent of 0.5-second cotton yellowed more than those containing 16 per cent of the same cotton; the former, containing pigment transparent to ultraviolet light, were more durable than the latter, but with pigments opaque to ultraviolet light, the enamels containing the lower cotton content were the more durable. Increasing the gum content from 1.5 to 3 per cent decreased durability and increased gloss when dammar gum was used, but with ester gum both these properties were increased. Comparative tests of tricresyl phosphate and triphenyl phosphate showed little preference except when the tests were run at 48°C., when the films containing the latter rapidly became weak and brittle, apparently as a result of crystallization of the plasticizer. The addition of clear lacquer to a pigmented lacquer in the finishing coats, or a finishing coat of clear lacquer or of varnish, always decreased the durability of the pigmented lacquer job. A wax finish stands up better than a buff finish.

Von Mühlendahl and Schulz[152] studied the influence of plasticizers on nitrocellulose under the influence of light and heat, judging it from the color of a mixture of equal amounts of the two products when heated to 100°C. or exposed to the rays of a quartz lamp.

According to Merz,[153] weathering under a carbon arc, and the results of a baking-bending test of a series of red, white and black lacquers with varying quantities of ester gum, gave the best correlation with outside weathering.

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[150] Denham, A. F., *Automotive Industries*, **56**, 544 (1927).

[151] Nelson, H. A., *Can. Chem. Met.*, **10**, 11 (1926); *Chem. Abs.*, **20**, 995 (1926).

[152] Von Mühlendahl, E., and Schulz, H., *Farbe und Lack.* 276 (1927); *Chem. Abs.*, **22**, 3055 (1928).

[153] Merz, O., *Farben Ztg.*, **36**, 316, 362 (1930); *Chem. Abs.*, **25**, 608 (1930).

Studies of the ultraviolet light absorption by lacquer films and their constituents indicated that within the range present in sunlight, all of the absorption by an ordinary lacquer is due to ester gum with lesser absorption by such plasticizers as tricresyl phosphate and castor oil.[154] The failure of ordinary lacquer films is ascribed to excited ester gum molecules transferring their energy to neighboring nitrocellulose molecules. Avoidance of the use of ingredients opaque to the ultraviolet of sunlight should improve the light resistance. In general agreement with this, Münzinger [155] observed that nitrocellulose films containing 29 different softeners were all more sensitive than the nitrocellulose alone. Castor oil and tritolyl phosphate caused the greatest and glycol monomethylphthalate the least alteration on exposure. Münzinger also tabulated the changes in fluorescence colors resulting from the exposure.

The Elektrizitätswerk Lonza [156] produces a varnish containing diphenylamine to retard the absorption of ultraviolet light by nitrocellulose films.

Dykstra [157] uses crotyl cellulose or allyl cellulose and a drier, such as cobalt oleate, for lacquers which may be baked. Ultraviolet light may be used for insolubilizing the films of crotyl cellulose. Ethylcellulose films approximate acetylcellulose films in transparency and light resistance. Prolonged exposure of ethylcellulose films to ultraviolet light at high temperatures depolymerizes the cellulose molecule with lowering of the viscosity.[158]

Since the cellulose acetate lacquers are more resistant to light than cellulose nitrate lacquers, it has been proposed to coat the latter with the former.[159] However, cellulose acetate does not absorb the rays which decompose the nitrate in the lower layers so that such protection is not complete. To overcome this, many additions to the cellulose acetate layer have been suggested to render them opaque. The addition of 7 oz. of stannic acid per gallon has been proposed for use in protective coatings for airplane wings by Doerflinger. In the preparation of an actinism-proof cellulose ester composition, Clewell [160] coats transparent sheets of pyroxylin on both sides with a colorless transparent oil-resin varnish, *e.g.*, a copal-linseed oil mixture impervious to ultraviolet light.

In the cellulose acetate of other overcoatings, Staud and Murray [161] use about 2 per cent of phthalic acid neutral esters of monoethers of hydroquinone and their homologs. In the production of laminated glass, two layers of overcoating are placed on each side of the cellulose nitrate film which is then incorporated between two sheets of glass. (It was also claimed that crystallization within the cellulose ester sheets produced beautiful effects and that such materials might be useful in the manufacture of toilet articles, novelties, etc.)

Many other organic substances have been proposed for this purpose, including polycyclic hydrocarbons or their derivatives, such as phenanthrene, naphthalene, chloronaphthalene, anthracene or *p*-amino-benzoic acid, phthalimide, nitroanisole, nitrobenzene, quinaldine, benzyl benzoate, glycerol butyl phthalate and β-methoxymethyl phthalate, dibenzofuran, diphenylbenzene, diphenylguanidine, xanthydrol or phthalanil.[162]

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[154] Davey, W. P., Duncan, D. C., and Wiggam, D. R., *Phys. Rev.*, 35, 1423 (1930); *Ind. Eng. Chem.*, 23, 904 (1931).

[155] Münzinger, W. M., *Chem. Ztg.*, 56, 851 (1932).

[156] Swiss P. 128,476, May 25, 1927, to Elektrizitätswerk Lonza; *Chem. Abs.*, 23, 2840 (1929).

[157] Dykstra, H. B., U. S. P. 1,920,297, Aug. 1, 1933; *Chem. Abs.*, 27, 4943 (1933).

[158] Ushakov, S. N., Shneer, I. M., Demina, E. N., and Ijboldina, *Rev. gén. mat. plastiques*, 13, 341 (1937); *Chem. Abs.*, 32, 3603 (1938).

[159] Application of Steel, P. C., U. S. Serial No. 425, 353. Cited by Staud, C. J., and Murray, T. F., Jr., U. S. P. 1,950,907.

[160] Clewell, J. H., Jr., U. S. P. 1,647,435, Nov. 1, 1927, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 22, 317 (1928).

[161] Staud, C. J., and Murray, T. F., U. S. P. 1,950,907, March 13, 1934; *Brit. Chem. Abs.*, B, 161 (1935).

Vanadium, cerium or titanium salts of a half ester of phthalic acid,[163] as well as triphenyl compounds of antimony or bismuth have also been suggested for this purpose.[164] Dreyfus [165] used a topcoat of phenol-furfural resin. This resin film is dried and converted to the insoluble, infusible state by baking, exposure to sunlight or ultraviolet light. Bradshaw [166] incorporates an iron or cobalt salt of naphthenic acid or a resin acid. Organic or inorganic compounds of copper may be added to purified benzylcellulose used as a basis for transparent films, sheets or plastics to render them resistant to the action of light and heat.[167]

According to Cofman and de Vore,[168] the wave-length most effective per quantum absorbed in causing the acid decomposition of nitrocellulose is about 3100A. It was to prevent the passage of this wave-length that most of the materials listed above were introduced. The observation by Rayleigh that celluloid containing malachite green becomes red when exposed to sunlight may be explained as due to the action of the liberated nitrogen oxides on the dye. Trevy [169] finds the light-yellowing of celluloid films most intense under wave-lengths between 3000 and 3500A.[170] Traces of metals may increase the yellowing. Durophen lacquer 218 V of the firm of Kurt Albert is completely opaque to ultraviolet light of wave-lengths shorter than 4000A even in thin layers. In the visible range, it transmits light increasingly toward the red end of the spectrum.[171]

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[162] British P. 371,901, Oct. 24, 1930, to Eastman Kodak Co.; *Chem. Abs.*, **27**, 3094 (1933); Staud, C. J., U. S. P. 1,958,683; *Chem. Abs.*, **28**, 4614 (1934); Murray, T F., U. S P. 1,958,711; *Chem. Abs.*, **28**, 4615 (1934); U. S. P. 1,976,359; *Chem. Abs.*, **28**, 7562 (1934); Canadian P. 339,837, March 6, 1934; U. S. Patent 2,043,805; Richardson, E., and Staud, C J., U. S. P. 1,958,714-5, *British Chem Abs.*, **B**, 278 (1935); U. S. P. 2,017,165; *Brit. Chem Abs.*, **B**, 1109 (1936); Staud, C. J., and Murray, T. F., U. S. P., 1,994,596; *Chem. Abs.*, **29**, 3182 (1935); Kocher, N. S., U. S. P., 1,973,488; *Chem. Abs.*, **28**, 7043 (1934).

[163] Salzberg, P., U. S. P. 1,965,608; Canadian P. 333,043, June 6, 1933; *Chem Abs.*, **27**, 4428 (1933).

[164] Murray, T. F., U. S. P. 1,969,473, *Chem Abs.*, **28**, 6329 (1934).

[165] Dreyfus, C., U. S. P. 1,964,039, June 26, 1934; *Brit. Chem Abs.*, **B**, 402 (1935).

[166] Bradshaw, H., U. S. P. 1,962,132; *Chem. Abs.*, **28**, 4904 (1934).

[167] French P. 795,880, March 24, 1936, to Soc. des usines chimiques Rhone-Poulenc, *Chem. Abs.*, **30**, 5690 (1936).

[168] Cofman, V., and de Vore, H. B , *Nature*, **123**, 87 (1929).

[169] Trevy, P., *Rev. gen. mat. plast.*, **13**, 60, 131 (1937); *Brit. Chem. Abs.*, **B**, 767 (1937).

[170] See also Report of Paint and Varnish Research Lab., Berlin, *Farben Ztg.*, **42**, 667 (1937); *Brit. Chem. Abs.*, **B**, 1088 (1937).

[171] Heyne, G., and Schön, M., *Angew. Chem.*, **49**, 784 (1936); *Chem. Abs.*, **31**, 321 (1937).

Chapter 31

Rubber

The absorption of ultraviolet radiations by rubber dissolved in pure hexahydrotoluene has been studied by Scheibe and Pummerer.[1] (See Figure 127.) Of samples of rubber from latex treated with alkali, rubber from non-coagulated latex, and "solrubber," the curves of the latter were believed most closely to approximate the absorption of rubber hydrocarbon. Gutta-percha gave a curve of similar type. Kröger and Staude [2] found that isoprene and various samples of rubber exhibit only continuous absorption. Synthetic rubber made from isoprene is more transparent than isoprene itself in the same thickness. The transparency of both synthetic and natural rubber increases with stretching,[3] presumably on account of some molecular change. Rubber vulcanized with sulfur chloride is much less transparent.[4]

POLYMERIZATION AND DEPOLYMERIZATION

Deresinized, colorless gutta-percha on exposure to ultraviolet light becomes more opaque and brittle, although still completely soluble in benzene.[5] This change has been assumed to be due to a transformation into a crystalline form, the existence of which has been demonstrated microscopically. Kirchhof [6] states that experiments by Porritt [7] indicated that a benzene solution of rubber slowly changes to a gel on exposure to ultraviolet light. Kirchhof found that this could be observed only in a very small volume of solution. With larger volumes depolymerization apparently occurred with a lowering of the viscosity. There have been many subsequent observations of the reduction of the viscosity of rubber sols by ultraviolet light.[8]

During this alteration of the viscosity of crude rubber solutions, the molecular polarization is not markedly affected, according to Kambara.[9] Garner [10] found that the reduction in viscosity during irradiation occurred particularly in solutions from which oxygen was excluded. On evaporation, there was obtained a depolymerized rubber which readily absorbed oxygen. Ordinarily, however, light and air cause both an oxidation and an increase in tackiness as judged by changes in viscosity. Garner concluded that the effect of light is partly polymerization and partly depolymerization. The latter predominates in an ordinary atmosphere. In nitrogen with but little oxygen, the rubber is in part rendered insoluble. The relative effects of various antioxidants in retarding the decrease in viscosity of irradiated rubber stands in no simple relation to their effects on actual oxidation. By favoring the formation of an insoluble polymer on the surface of exposed rubber, antioxidants may, indeed, accelerate the loss of surface tackiness.

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[1] Scheibe, G., and Pummerer, R., *Ber.*, **60**, 2163 (1927).

[2] Kröger, M., and Staude, H., *Gummi-Ztg.*, **43**, 22 (1928); *Chem. Abs.*, **23**, 306 (1929).

[3] For x-ray data on crystals in stretched rubber, see Clark, G. L., *Ind. Eng. Chem.*, **18**, 1131 (1926).

[4] For the Raman spectrum of rubber, see Gehman, S. D., *J. Am. Chem. Soc.*, **57**, 1382 (1935).

[5] Kirchhof, F., *Kautschuk*, **4**, 254 (1928); *Chem. Abs.*, **23**, 1525 (1929).

[6] Kirchhof, F., *Kautschuk*, 28, 1927; *Chem. Abs.*, **21**, 1377 (1927).

[7] Porritt, B. D., *India Rubber J.*, **60**, 1159 (1920); *Chem. Abs.*, **15**, 1230 (1921).

[8] Gallay, W., *Canadian J. Res.*, **7**, 671 (1932); *Chem. Abs.*, **27**, 1561 (1933). See, however, Dogadkin, B., and Lavrenenko, M., *Kautschuk*, **9**, 97 (1933); *Chem. Abs.*, **27**, 4953 (1933).

[9] Kambara, S., *J. Soc. Chem. Ind. Japan*, **39**, 138 (1936); *Chem. Abs.*, **30**, 6298 (1936).

[10] Garner, T. L., *Trans. Inst. Rubber Ind.*, **4**, 413 (1929); *Brit. Chem. Abs.*, **B**, 445 (1929).

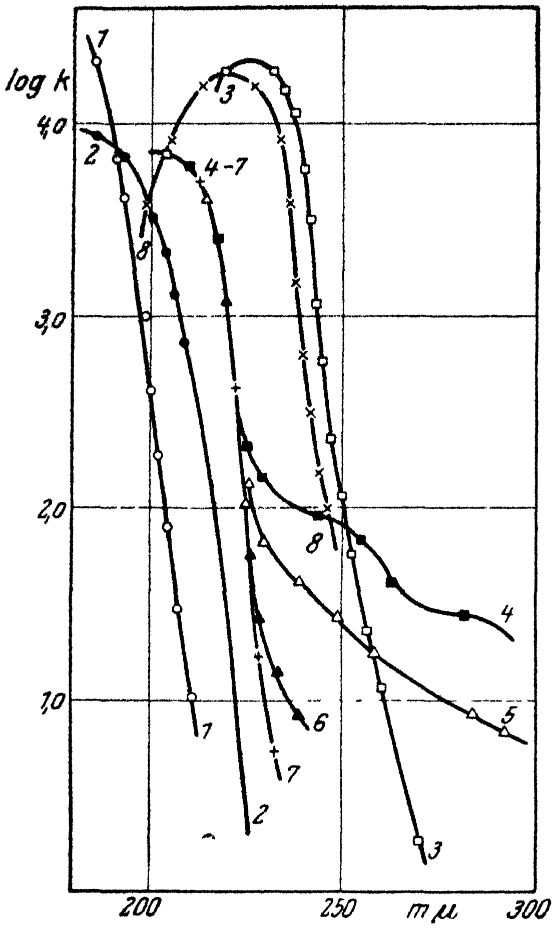

FIGURE 127.

Absorption of Latex, Sol-Rubber and Related Compounds (Scheibe and Pummerer, *Berichte der deutschen Chemischen Gesellschaft*).

1. Diallyl
2. Trimethylethylene
3. Dimethylbutadiene
4. Latex purified with NaOH and coagulated
5. Latex, uncoagulated
6. Latex, purified with NaOH
7. Sol rubber
8. Isoprene

Mojen[11] found that no change in the viscosity of ordinary rubber solutions containing monochloracetic acid occurs in light when oxygen is rigorously excluded. The same was true also of balata solutions containing acetic acid or its chlorine substitution products. But with oxygen present, the rubber sols changed to an insoluble product even in darkness. The protective power of the natural antioxidants, which are probably basic, is destroyed when they are combined with acids. A benzene solution of purified gutta-percha irradiated in an atmosphere of hydrogen gave on evaporation a white, unctuous, fragile product which melted to a limpid oil at 90°C. On cooling, the latter gave a tough product like the original gutta-percha, so that heating was assumed to have destroyed the crystalline struc-

[11] Mojen, H. P., *Kautschuk*, 13, 39 (1937); *Chem. Abs.*, 31, 5214 (1937).

ture. The melting point of the microcrystals of the irradiated material was believed to be lower than that of the crystals which are obtained in films formed by evaporation of nonirradiated solutions. The product left after the evaporation of the benzene from an irradiated solution redissolved to a clear solution in benzene, if the irradiation is conducted in hydrogen; but irradiation of a film with air present gives a product which is partly insoluble. Such effects are not observed in the case of rubber. The different behavior of gutta-percha is ascribed to its higher state of polymerization.

No change in the unsaturation of a 1-per cent solution of pale crepe rubber can be detected by a modified Wijs method after irradiation under carbon dioxide in a quartz flask for 28 to 45 hours by a quartz mercury-vapor arc.[12]

The ultraviolet radiations present in sunlight tend to polymerize rubber, isoprene and styrene, especially in the presence of sensitizers (compare the cinnamic acids, Chapter 25).[13] Ether solutions of rubber under nitrogen in sealed tubes generally gelatinize when exposed to sunlight, but the length of time required, sometimes weeks, varies so greatly that this is not a practicable method of bringing about gelation. The light rubber obtained by evaporating the ether gel is entirely insoluble in ether if the illumination has been sufficiently prolonged. On milling rolls, it gradually becomes ether-soluble again, but it differs from gel rubber in that the addition of diethylamine, piperidine, etc. does not make it ether-soluble. Its iodine number is 94 to 98 per cent of that of the original sol rubber. Apparently the chemical effect of the irradiation is a polymerization involving only from 2 to 6 per cent of the double bonds. The gelation can be regulated and reproduced at will by the use of various sensitizers containing a carbonyl group. With eosin, gelation can be demonstrated in about ten minutes in quartz under a mercury arc, and even 0.2 per cent solutions of rubber in carbon tetrachloride can be made to gel. It is the longer wave lengths between 2800 and 3150A which are believed effective. Methylene blue and malachite green offered no advantages over eosin. Diphenylketone (3150 to 4000A) and benzanthrone (3150 to 4200A) are also effective. Benzaldehyde also produces gelation, but with it and with acetaldehyde the conditions do not seem as simple as with the ketones. Methylbenzyl oxide proved to be moderately effective, but aliphatic esters and such colored hydrocarbons as perylene had no action. The same sensitizers also bring about the gelation of liquid isoprene and isoprene emulsions in soap solutions in glass. The resulting isoprene rubbers give iodine numbers of 94 to 99 per cent of the theoretical, but with evolution of considerable quantities of hydrogen iodide.

Liquid styrene is readily polymerized to solid styrene resin in glass in the presence of sensitizers in several days of exposure to a 200-watt lamp at room temperature. In the presence of diphenyl ketone or benzanthrone at 60-70°C. and with a 500-watt lamp, the change is complete in a few hours. The reaction proceeds two to three times as rapidly under cylinder nitrogen containing some oxygen as it does under pure nitrogen. Since it is oxygen in the gas phase that is effective, it may be assumed that gelation begins at the gas-liquid interface. Such antioxidants as hydroquinone inhibit the reaction. The presence of "active oxygen" during the irradiation of diphenyl ketone, phenylmethyl ketone and even of diethyl ketone was shown by means of a benzidine-sodium chloride solution. Iron compounds (ferric chloride, ferric acetylacetonate, iron pentacarbonyl) do not accelerate the photogelation of rubber solutions. Kirchhof[14] also noted that when a benzene solution of phosphorus is added to a rubber solution before exposure, irradiation produces a gel similar to that produced with dilute sulfur chloride. This gel is formed even in rubber solutions which have previously been depolymerized by light. If rubber-phosphorus solution which has been exposed to light but not gelatinized is evaporated and extracted with acetone, the resulting rubber is similar in physical properties to rubber vulcanized with sulfur chloride. Similarly treated samples in which no phosphorus had been added gave only a weak, tacky product. There is no change apparent in phosphorus-containing benzene solutions of rubber exposed in carbon dioxide to daylight at 70-75°C. Without rubber present, benzene solutions of yellow phosphorus deposit red phosphorus on exposure to ultraviolet light or to sunlight, but rubber has a protective action so that in its presence this reaction does not occur. The phosphorus photovulcanization occurring in rubber solutions in ultraviolet light resembles sulfur vulcanization in that gel formation is greatly accelerated by zinc xanthate.

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[12] Fisher, H. L., and Gray, A. E., *Ind. Eng. Chem.*, **18**, 414 (1926).

[13] Pummerer, R., and Kehlen, H., *Ber.*, **66B**, 1107 (1933); *Chem. Abs.*, **27**, 6018 (1933).

[14] Kirchhof, F., *Kautschuk*, **28**, (1927); *Chem. Abs.*, **21**, 1377 (1927).

In latex, polymerization by quinone is readily aided by irradiation.[15] At 90°C., air causes depolymerization, even in light. When portions of quinone and latex were irradiated separately and mixed in darkness, no enhanced polymerization resulted. It also does not result from the irradiation of latex alone. The photochemical polymerization is not inhibited by an excess of hydroquinone, but it is greatly reduced by an excess of a dark brown oxidation product of quinone, which may compete in absorbing the effective light. When a solution of rubber in benzene containing quinone is irradiated in the presence of air, there is marked depolymerization at room temperature, but irradiation at −80°C. leads to enhanced polymerization.

The addition of an inorganic cobalt salt or of cobalt resinate to a benzene solution of rubber causes rapid depolymerization, which is accelerated by air and light.[16] The effects of many antioxidants and accelerators upon the development of tackiness in rubber when exposed to a General Electric S-1 lamp have been determined by Blake and Bruce.[17]

Irradiation of chloroprene by the 2537A line leads, after a long induction period, to a polymerization in the condensed phase. A dark polymerization subsequently ensues.[18] Butadiene shows little tendency toward photopolymerization and the quantum yield in the mercury-sensitized reaction is only unity. This compound admixed with methyl methacrylate inhibits the photopolymerization of the latter, which in the absence of this inhibitor has a quantum yield of about one hundred.

No indication of a *cis-trans* transformation by ultraviolet could be found by Meyer and Ferri,[19] although they state that light effects a kind of "vulcanization" by irregular polymerization. When solutions of 1 g. and 2.5 g. of coagulated latex in 100 cc. of cyclohexane were irradiated in a quartz flask in oxygen for ten hours at 5 cm. from a 300-watt quartz mercury arc, elastic gels insoluble in solvents were formed. These were similar to products obtainable by the addition of small amounts of sulfur chloride. Dry gels formed in the absence of oxygen had the mechanical properties of a feebly vulcanized rubber. It is believed that in such gels, the original rubber hydrocarbon chains are oriented in a three-dimensional network through the establishment of valence bonds transversely and between the double bonds.

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[15] Spence, D., and Ferry, J. D., *J. Am. Chem. Soc.*, **59**, 1648 (1937).

[16] Krauz, C., and Franta, I., *Rubber Tech. Conf., London, Preprint No. 13* (May, 1938); *Chem. Abs.*, **32**, 8169 (1938).

[17] Blake, J. T., and Bruce, P. L., *Rubber Tech. Conf., London, Preprint No. 21* (May, 1938); *Chem. Abs.*, **32**, 8833 (1938).

[18] Bolland, J. L., and Melville, H. W., *Rubber Tech. Conf., London, Preprint No. 90*, May, 1938; *Chem. Abs.*, **32**, 8396 (1938).

[19] Meyer, K. H., and Ferri, C., *Helv. Chim. Acta*, **19**, 694 (1936); *Chem. Abs.*, **30**, 6601 (1936); *Rubber Chem. Tech.*, **9**, 570 (1936).

It has been observed that gasoline rubber cements exposed to sunlight in glass in most cases became solvent-thin, although in a few cases gels formed.[20] Carbon tetrachloride cements all formed rigid gels. The behavior of the latter is ascribed to a curing by ultraviolet light and by chlorine resulting from decomposition of the solvent. Similar results were obtained at a slower rate in diffused light. Protection of the gasoline cements by red filters greatly prolonged the time required for them to thin. The higher the rubber content of a cement, the smaller is the change in its viscosity.

VULCANIZATION

Victor Henri is credited by Helbronner with having used ultraviolet rays as early as 1909-10 for the vulcanization of films made from solutions of rubber. Rubber solutions vulcanized by ultraviolet are stated by Helbronner[21] to be insoluble in the original solvent after they have been dried. Bernstein[22] proposed vulcanizing rubber solutions containing sulfur by exposing them to the action of ultraviolet rays produced by a quartz mercury-vapor lamp, the solutions being spread on a moving metallic ribbon. A solution of rubber in benzene containing 6 per cent of rubber, and sulfur equal to 10 per cent of the rubber, when exposed in a film 0.5 mm. thick required forty to fifty seconds for vulcanization. Ordinary or high temperatures, pressure or vacuum, air or inert gas atmospheres, may be used. Bernstein[23] evaporated a xylene solution of Hevea plantation rubber with 6 per cent of sulfur to a thin film on a transparent quartz plate and covered it with another quartz plate. This was exposed on both sides for forty minutes at a distance of 15 cm. to the rays from a Heraeus lamp of three amperes and 110 volts. The film then possessed the properties of vulcanized rubber and contained 2.56 per cent of combined sulfur. Other experiments showed that the percentage of combined sulfur increased with the time of exposure to the rays. The deterioration of vulcanized rubber on exposure to ultraviolet rays, observed by Henri, is considered to be chiefly due to "after-vulcanization." Stern[24] states that the vulcanization is accompanied by some depolymerization. Ostromuislenski[25] believed that, in the absence of air, the rays activate sulfur by converting it into thiozone. The vulcanization is then affected partly by the latter and partly by the ozone formed simultaneously.[26]

According to Pohle,[27] irradiation of a supersaturated solution of sulfur in rubber, prepared by heating, results in separation of the sulfur. The effect, which is due to the violet and blue rays, can be followed ultramicroscopically by a quartz ultracondenser. The number of particles depends on the intensity of the light and on the time of exposure. Long exposures or high intensities give dense, fine, blue dispersed fogs and short exposures give a smaller number of more rapidly growing droplets. The smallest effect, one to five particles, resulted from an exposure of .01 second to a 5-ampere lamp. The sulfur particles are apparently liquid. The sensitivity to light is diminished by the presence of substances which absorb blue or violet rays. The sulfur then appears only at the surface. This effect of light is also inhibited by even the slightest vulcanization of the rubber, and it can therefore serve as an indication of the vulcanization process. The effect is observed as far below the surface as the light penetrates.

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[20] Novotny, C. K., *Ind. Eng. Chem.*, **26**, 170 (1934).

[21] Helbronner, A., *India Rubber World*, 130 (**1914**); note also *Compt. rend.*, **138**, 1343 (1914); *Chem. Zentralbl.* 326, (**1914**); *Kolloid Z.*, 4, (**1913**); French P. 460,780, July 26, 1913.

[22] Bernstein, G., British P. 17,195, July 26, 1913; U. S. P. 1,240,116, Sept. 11, 1917.

[23] Bernstein, G., *J. Frank. Inst.*, 345, **1913.** Note also Helbronner, A., and Bernstein, G., *Rubber Ind.*, 156 (**1914**); *Caoutchouc et Gutta-Percha*, **12,** 8720 (1915). Green, H., *Ind. Eng. Chem.*, **17,** 802 (1925) has used the ultraviolet microscope in connection with a study of vulcanized latex globules; see also Lucas, F. F., [*Ind. Eng. Chem.*, **30,** 146 (1938)] for observations on untreated latex. Note also Gray, G. W., *Technology Rev.*, **40,** 172, 188, 190, 192 (1938).

[24] Stern, E., *Chem. Ztg., Rep.* 422 (1913).

[25] Ostromuislenski, I. I., *J. Russian Phys. Chem. Soc.*, **47,** 1892-1898 (1915); *J. Soc. Chem. Ind.*, 370 (**1916**).

[26] Meyeringh, D. J., and Wijnand, P. C., British P. 208,167, Dec. 24, 1924; *Chem. Abs.*, **18,** 1589 (1924).

[27] Pohle, H., *Naturwiss.*, **15,** 162 (1927); *Chem. Abs.*, **21,** 1904 (1927).

During the vulcanization of rubber by phosphorus in ultraviolet light, there appear after prolonged illumination of the optically empty rubber-phosphorus-benzene system, glistening phosphorus particles 0.5 to 2.1 μ in diameter.[28] This formation of nuclei by ultraviolet has its analogy in the transformation of yellow to red phosphorus. A similar turbidity appeared on ultraviolet illumination of a carbon disulfide solution of sulfur containing piperidine pentamethylenedithiocarbamate.

Kirchhof also states [29] that vulcanization of rubber in ultraviolet light by trinitrobenzene or picric acid, especially the former, yields results comparable with those of cold vulcanization. These products, like ordinary vulcanizates, show strong absorption of ultraviolet radiations.

In producing lustrous spread rubberized material, Ditmar [30] spreads the material in the usual way with a benzene solution of a mixture containing crêpe rubber 100 parts, colloidal sulfur 3.5 parts, tetramethylthiuramdisulfide 2 parts, Sulzin (*i.e.*, zinc sulfate-5 NH_3), 7 parts, anhydrous sodium thiosulfate 2 parts, selenium red 1.8 parts and titanium oxide 2 parts. It is then led directly under a battery of quartz mercury lamps, the exposure being for five minutes at a distance of 8 cm. Complete vulcanization results with the production of a non-tacky rubber surface of high lustre.

It was necessary to carry out the process of Bernstein [31] in an inert gas or *in vacuo* to prevent oxidation by the ozone. But when tetramethylthiuramdisulfide is used as an accelerator to minimize the curing time and exposure, and with selenium red as a protective agent, it is possible to cure the spread material in air. Ditmar [32] also showed that ultraviolet radiation has itself an oxidizing action on accelerated rubber mixtures which predominates over the vulcanization. Therefore, from a practical point of view, satisfactory vulcanization is possible only when a red or yellow protective pigment, such as selenium red, is added. With an activator like zinc oxide present in an accelerated mixture, ultraviolet radiation brings about vulcanization in a short time. The duration of the exposure must be carefully controlled to prevent oxidation, under-curing or over-curing. Ultraviolet radiation has the most favorable effect on rubber mixtures accelerated by tetramethylthiuramdisulfide and containing an activator. Surface vulcanization is complete in four and a half minutes without oxidation even in the absence of a protective red pigment.

Surface vulcanization by light is regarded as a true vulcanization process since it has been proved that sulfur must be present. It is believed that the sulfur is activated by the radiation and then enters into reaction with the rubber.[33] Ditmar and

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[28] Kirchhof, F., *Kautschuk*, 184 (1927); *Chem. Abs.*, 21, 2819 (1927).

[29] Kirchhof, F., *Gummi-Ztg.*, 44, 252 (1929); *Chem. Abs.*, 24, 750 (1930).

[30] Ditmar, R., *Gummi-Ztg.*, 43, 1172 (1929); *Brit. Chem. Abs.*, B, 294 (1929); *Chem. Abs.*, 23, 2602 (1929).

[31] Bernstein, G., German P. 262,708, 1912.

[32] Ditmar, R., *Gummi-Ztg.*, 43, 1172, 2325 (1929); *Chem. Abs.*, 23, 2602, 4374 (1929).

[33] Ditmar, R., and Grünfeld, O., *Gummi-Ztg.*, 43, 2801, 2859 (1929); *Chem. Abs.*, 23, 5612 (1929).

Grünfeld find that, when about 3 per cent of sulfur is present, the addition of organic accelerators can be completely dispensed with. Indeed, many organic accelerators may have an unfavorable action. In most cases, Vulkan colors give excellent shades of color under these conditions, and in combination with other organic and inorganic colors such as selenium red or methylene blue, all kinds of colors and tones can be obtained. In general, ultraviolet vulcanization can be effected in four to eight minutes at 20-90° C., depending upon the support on which the sample rests, the shortest times being obtained on glass. This influence of the support apparently depends upon its heat conductivity and heat capacity, for the higher the temperature prevailing during the process, the more rapid its rate.

Formulas of blue, green, orange, red and brown rubber mixtures which will cure in seven minutes at a distance of ten cm. from the ultraviolet source are given by Ditmar and Preusze.[34]

In patents of the Goodyear Tyre and Rubber Co.[35] the appearance and dirt-resisting qualities of vulcanized rubber are claimed to be improved by exposure to ultraviolet radiation.

On the assumption that the increase in the electrical conductivity of hard rubber on exposure to light and air is a result of the formation of a surface film containing acid, Fry and Porritt[36] carried on experiments to ascertain the mechanism of its formation. It was found that hydrogen sulfide is evolved, the rate of evolution being the greatest in direct sunlight. This may, however, be the result of thermal rather than light action. This evolution of hydrogen sulfide results from a decomposition of the rubber-sulfur compound and occurs in the absence of free sulfur, resins, oxygen and water vapor. Its rate increases with a rise of temperature.

Ultraviolet vulcanization has been employed in the production of surface designs on rubber.[37] A surface of a rubber sheet to be etched is vulcanized by the action of ultraviolet rays or by sulfur chloride, a design is formed on the surface and an etch-resist may be incorporated with the inked parts. A mixture of nitric acid and potassium dichromate is used for etching and the etched sheet is washed with acetone or alcoholic soda solution. Silex and fat-containing fillings should not be present in the rubber.

Rimpel and Hermann[38] state that when strong reducing agents, such as a light-sensitive silver bromide gelatin, are mixed into the rubber, it is possible to form designs or pictures directly by exposure to the light. They do not agree with the suggestion of Defries and Naunton that a discoloration on irradiation is the result of an over-vulcanization produced by light on the surface. When four mixtures, each containing rubber, lithopone and zinc oxide, and the first also sulfur; the second, accelerator; the third, sulfur and accelerator, and the fourth, no addition, were exposed to sunlight for thirty minutes, the first and fourth mixtures remained unchanged, but the second and third became discolored to an equal extent. This indicates that the discoloration depends only on the accelerator and has no direct relation to the state of vulcanization. The accelerator thus behaves like a reducing agent.

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[34] Ditmar, R., and Preusze, K. H., *Caoutchouc & gutta-percha*, **26**, 14,762 (1929); *Gummi-Ztg.*, **43**, 2749 (1929); *Brit. Chem. Abs.*, **B**, 863 (1929); *Chem. Abs.*, **24**, 749 (1930).

[35] British P. 404,120, Nov. 10, 1932, to Goodyear Tyre and Rubber Co; French P. 749,642, July 27, 1933; *Chem. Abs.*, **28**, 685 (1934).

[36] Fry, J. D., and Porritt, B. D., *India Rubber J.*, **78**, 307, 309 (1929); *Chem. Abs.*, **23**, 5613 (1929).

[37] British P. 241,542, Oct. 14, 1924, to Soc. d'Exploitation des Procedes d'Impression Sardou; *Chem. Abs.*, **20**, 3590 (1926).

[38] Rimpel, H., and Hermann, P., *Gummi-Ztg.*, **43**, 2270 (1929); *Chem. Abs.*, **23**, 4370 (1929); German P. 448,972; see also Defries, R., and Naunton, W., *Trans. Inst. Rubber Industry*, **4**, 298 (1928); *Chem. Abs.*, **23**, 2068 (1929).

Fluorescence of Accelerators. Various accelerators are readily distinguished by their characteristic fluorescence colors in filtered ultraviolet light. When present alone in pale crêpe, some of them may be detected by this method.[39] Even when some other ingredients, such as sulfur, zinc oxide, magnesia, lead oxide, etc., are present, it is possible, in some cases, to distinguish a characteristic appearance. However, with several ingredients present, the fluorescent effect varies with the different combinations, and only when the composition of the mixture is known can the method be employed for the detection of accelerators. Characteristic colors are also obtained after vulcanization, although they are different from those observed in the same mixtures prior to vulcanization.[40] The approximate quantity may be judged within ±5 per cent if the fluorescent light from filtered ultraviolet is passed through an actinometer containing a triphenylmethane dye. Ditmar[41] has listed the fluorescence colors of a number of accelerators. The change of fluorescent color on prolonged irradiation is also of significance.

Nagle[42] employed this method for the study of the pigments used in the industry. In the examination of eight grades of zinc oxide mixed with glycerol, one appeared light green, one light gray-green, one light green-gray, two orange-buff, one bright apple-green, one pale dull violet and one deep violet. After having been kept ten minutes at a white heat, all were green. The same distinctive shades were visible in rubber mixtures when a small proportion was used in vulcanizing the rubber with sulfur, accelerator and lithopone. Even when the rubber mixtures were made dark gray by the addition of carbon black, the individual samples containing zinc oxide could still be distinguished. In lithopones, the range of colors was not so great, the samples appearing deep violet, pale violet, brown or almost white. An examination of rubber imperfectly mixed with zinc oxide and lithopone revealed the characteristic colors of the two pigments and indicated the possibility of determining the distribution of powders in rubber mixtures. The lithopones which appeared deep violet were the most nearly sunproof. Those which appeared white darkened the most rapidly. In filtered ultraviolet light, however, the latter were resistant, indicating the radiation responsible for the darkening to be of wave-length shorter than that transmitted by the filter used (3300-3900A). Mineral oils and Vaseline were fluorescent and phosphorescent, coal-tar showed a faint, yellow-brown fluorescence and sulfur assumed a bronze color. In the form of bloom, it can be readily distinguished by this method. Addition of 1 per cent of coal tar to a black rubber mixture changed its appearance in filtered ultraviolet light from very dark violet to gray-blue. Various tire sections appeared violet, brown-violet, blue, green, yellow and brown-red, since various other added substances exhibited characteristic fluorescences.[43]

Kirchhof[44] reported similar observations, but differed from Nagle in believing the purest grade of zinc oxide to be sulfur-yellow. Since zinc sulfide gives a bright orange color, the fluorescence of lithopone varies with its zinc sulfide content. Among aliphatic substances, vegetable and animal oils, fats and waxes and paraffin hydrocarbons show characteristic colors. Phenols and aromatic acids exhibit particularly bright colors, the intensity apparently increasing with the complexity of the ring. Nitro- groups weaken the fluorescence. Dyes, accelerators and antioxidants are also distinguished by characteristic colors in this manner. The differences in the appearance of various rubbers in filtered ultraviolet depend chiefly upon material which can be extracted by acetone. It was suggested that the method might be of value in following the natural or artificial aging of rubber mixtures by oxidation.

Ditmar[45] employed the method particularly for the study of accelerators. The color of mercaptobenzothiazole, for example, varied with the manufacturer. Kojima and Nagai[46] reported observations on 41 such substances. Morris[47] considered especially the substances important in American manufacture. The personal element plays a large part in the recording of the colors, so that it is necessary to have standard samples available for comparison Morris believed the color variation in samples of zinc oxide to be related to a certain extent to the particle size. Well-vulcanized rubber shows a yellow fluorescent color of fairly strong intensity, but decidedly undercured rubber fluoresces only slightly. Rubber loses its fluorescence almost completely after an hour in direct sunlight. For this change, oxygen is not essential. In general, no definite relation is apparent between the optimum physical properties of rubber and the intensity of its fluorescence.[48]

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[39] Ditmar, R., and Dietsch, W., *Chem Ztg* **52,** 388 (1928); *Gummi-Ztg.,* **42,** 1415 (1928).

[40] M. L. P., *Rev. gen. caoutchouc,* **6,** No. 53, 9 (1929); *Chem. Abs.,* **23,** 5612 (1929).

[41] Ditmar, R., *Chem Ztg.,* **52,** 730 (1928); see also Garner, T. L., [*India Rubber J.,* **77,** 31 (1929); *Chem. Abs.,* **23,** 1772 (1929)] for the identification of antioxidants by this method.

[42] Nagle, P. G., *Trans. Inst. Rubber Industry,* **3,** 304 (1927); *Chem. Abs.,* **22,** 1251 (1928).

[43] Nagle, P. G., *Rubber Chem. & Tech.,* **1,** 284 (1928).

[44] Kirchhof, F., *Kautschuk,* **4,** 24 (1928); *India Rubber J.,* **75,** 791 (1928); *Chem. Abs.,* **22,** 2291 (1928).

[45] Ditmar, R., *Caoutchouc & gutta-percha,* **28,** 15,685 (1931); *Chem. Abs.,* **25,** 6017 (1931).

[46] Kojima, K., and Nagai, I., *J. Rubber Soc Japan,* **2,** 260 (1930); *Chem. Abs.,* **25,** 3871 (1931).

[47] Morris, V. N., *Ind. Eng. Chem.,* **26,** 107 (1934).

Fluorescence tests may also be employed in judging the progress and uniformity of vulcanization. The light emitted by mixtures containing three to eight per cent of sulfur increases with the state of vulcanization. The fluorescence changes are accelerated by zinc oxide.[49] With ten per cent or more of sulfur, when semi-ebonites are formed, the fluorescence becomes brown-red and less intense. Undercured rubber mixtures, in general, show relatively weak fluorescence and overcured ones a strong fluorescence, greenish for rubber and sulfur mixtures and yellowish-green for accelerated mixtures. Excessive overcuring may make the fluorescence yellow. The fluorescence of Neoprene also increases during vulcanization without sulfur but less markedly than in the case of rubber. Oberto[50] has also described the changes in fluorescence of vulcanized rubber during aging, natural or artificial In the initial stages (one minute in sunlight), it changes to violet, even before an alteration of mechanical properties can be noted. Later it becomes more intense, finally changing to ochre or red, depending upon the sulfur content, at complete deterioration (ten hours of exposure). The presence of other substances may complicate the fluorescence effects.

Light and the Oxidation of Rubber

In reviewing this topic, Shepard, Krall and Morris[51] state that as early as 1865, Spiller[52] proved that oxygen functions in the change undergone by strained rubber in light. Burghardt[53] believed that light alone would injure perfectly good normal vulcanized rubber only when acting in conjunction with other destructive agents. Fickendey[54] showed that samples exposed to direct sunlight in sealed tubes in hydrogen, nitrogen and carbon dioxide remained unchanged for weeks, although rubber exposed under oxygen became sticky. Ahrens,[55] Peachy and Leon,[56] and Henri[57] considered sun-checking or sun-cracking an oxidation process aided by both light and heat.

Asano[58] observed that when rubber is exposed to ultraviolet light under carbon dioxide, nitrogen or hydrogen, it is converted into two products of much the same composition. One was a white, opaque, brittle, polymerized substance, insoluble in benzene. The other was a depolymerized, tacky product of reduced viscosity. Similar behavior was observed during exposures in air. Asano believed that radiations longer than 3100A had no significant effect, and that these physical and chemical changes were most rapid and profound under the influence of wave-lengths between 2250 and 2000A. Some dyes, however, sensitize rubber to longer wave-lengths. These changes were largely independent of oxidation, which occurred to a considerable extent only in sunlight, and caused tackiness, followed by brittleness. The ultimate products were insoluble in boiling benzene, chloroform, alcohol or acetone, and contained 14.6 per cent of oxygen. The action involved an initial depolymerization, with subsequent accelerated oxidation of the depolymerized product. The oxidation was induced by wave-lengths shorter than 5000A, and the depolymerization by longer wave-lengths. Elimination of the infrared rays by a water filter did not alter the action of sunlight. The intensity of light governed the rapidity of the changes. Asano also alluded to the deleterious action of ozone.

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[48] For a general review of fluorescence tests for rubber, see Hauser, E. A., and Le Beau, S., *Kautschuk*, **10**, 113 (1934); Krahl, M., *Kautschuk*, 159, 180 (**1927**).

[49] Oberto, *Gomma*, **1**, 157 (1937); *Chem. Abs.*, **32**, 3198 (1938).

[50] Oberto, S., *Rubber Tech. Conf. London, Preprint No 75*, May, 1938; *Chem. Abs.*, **32**, 8212 (1938).

[51] Shepard, N. A., Krall, S., and Morris. H. L., *Ind. Eng. Chem.*, **18**, 615 (1926).

[52] Spiller, J., *J. Chem. Soc.*, **18**, 44 (1865).

[53] Burghardt, C. A., *J. Soc. Chem. Ind.*, **2**, 119 (1883).

[54] Fickendey, E., *Kolloid Z.*, **9**, 81 (1911).

[55] Ahrens, F., *Kunststoffe*, **3**, 478.

[56] Peachy, S. J., and Leon, M., *J. Soc. Chem. Ind.*, **37**, 56T (1918)

[57] Henri, V., *Caoutchouc & Gutta-percha*, **7**, 4372 (1910).

[58] Asano, K., *India-Rubber J.*, **70**, 307, 347, 389, 395 (1925); *Chem. Abs.*, **19**, 3616 (1925).

Williams[59] definitely showed that 5 grams of emery-wheel buffings of a pure gum inner tube absorb oxygen more rapidly in sunlight (0.93 cc. per hour) than in darkness (0.13 cc. per hour). Light had, however, little effect upon unstrained strips of the same rubber. The success in the case of the buffings was due to the fact that the fresh surfaces clung together in such a manner as to keep the small particles in a strained condition.

It was claimed by de Jong[60] that in a quartz vessel exposed to sunlight in the Dutch East Indies, a benzene solution of crepe rubber absorbed a considerable volume of air. In later experiments with less intense sunlight in Holland, the same process occurred behind glass, but less rapidly. In eight days, 25 cc. of air were completely absorbed by 325 cc. of solution. de Jong claimed also that after six days of exposure in sealed tubes under nitrogen, a 1.05-per cent solution of rubber in benzene absorbed 2.5 per cent of nitrogen and that the absorption of this gas by the hydrocarbon from balata gutta-percha after purification with petroleum ether also occurs. However, nitrogen absorption by rubber has been denied by Howard and Hilbert.[61] Dogadkin and Panchenkov[62] observed that on irradiation of rubber solutions in nitrogen, the interfacial tension against water did not change. When irradiated in air, it was lowered and reached a constant value in two hours.

Bondy and Lauer[63] found, in agreement with Staudinger and Leupold, that rubber solutions do not autoxidize in darkness. In light, the solutions decomposed in the same manner whether or not the natural antioxidant was present. There was no decomposition when the exposures were made in nitrogen; only in light and air were positive results attained.

Williams[59] also showed that the exposure of strips of a vulcanized gray side-wall stock stretched to an elongation of 5 per cent, and exposed in air or oxygen (but not in evacuated tubes) to July sunlight daily for two weeks appeared slightly wrinkled. Upon releasing the strain, the wrinkled appearance became pronounced, showing that a non-elastic skin had formed on the surface. The weight had increased slightly. The skin had a glazed appearance, was almost inelastic but not brittle and was soluble in alcohol. The surface beneath appeared unchanged and no decrease in tensile strength could be observed. Light-colored rubber will form, in some cases, a pronounced skin in two days of exposure to the sun.

Tests by Williams with various colored filters indicated that the short wave-lengths of visible light from a tungsten lamp were most effective in producing surface oxidation. White light produced the heaviest skin. The amount of oxidation was directly dependent upon the intensity of the light. A mercury lamp placed ten inches from the strip elongated at about 10 per cent produced a pronounced surface oxidation in three hours. If, however, the mercury lamp is placed two to three feet from the strip no skin formed. Instead, after one or two hours, small cracks began to appear in the surface of the rubber. These continued to increase in size and number, but the surface between the cracks remained unchanged except on prolonged exposure. This type of oxidation, due it was believed to ozone, is characterized by extreme rapidity and by a negligible increase in weight.[64] In direct ozonizing tests, it was necessary to reduce the concentration of ozone to about one part in 50,000 of air in order to reduce the speed of cracking to a point at which observations could be accurately made. Surface oxidation appears to be to some extent an efficient protection against even a relatively high concentration of ozone, since this cracking was not observed in samples which had been exposed ten inches from the lamp. Checking can be retarded by catalyzing the surface oxidation by means of copper salts.[65] Compounds containing zinc oxide are more easily protected than pure gum type compounds.

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[59] Williams, I., *Ind. Eng. Chem.*, **18**, 367 (1926).

[60] de Jong, A. W. K., *Rec. trav. chim*, **51**, 133 (1932).

[61] Howard, L. B., and Hilbert, G. E., *J. Am. Chem. Soc.*, **59**, 214 (1937).

[62] Dogadkin, B., and Panchenkov, G., *Kolloid-Z.*, **65**, 350 (1933); *Chem. Abs.*, **28**, 1890 (1934).

[63] Bondy, H. F., and Lauer, G. G., *Ber.*, **66B**, 1611 (1933).

The basic components of the acetone-soluble material from rubber account for the antioxidant effect of both rubber and balata, according to Bondy and Lauer.[66] The acids, amino-acids and bases of the serum and phenols have a slight antioxidant effect. The neutral components and acid amides are inactive in this respect. Heating rubber or balata resin at 120°C. increases its protective action against ultraviolet light. Those rubber solutions which had the deepest brown color had the least tendency to autoxidize. Further experiments showed that a dye present in the rubber retards autoxidation by absorbing the active radiations. Tests of known dyes proved that some have a marked protective action by internal filtering, but others were only slightly protective.

Bondy,[67] irradiated purified balata in the solid state in air with sunlight and with ultraviolet light, determining the extent of autoxidation by measuring the viscosity of Tetralin solutions of a concentration corresponding to 0.2 molecule of isoprene, before and after irradiation, *i.e.*, by the general method of Staudinger. Rubrene and dehydrorubrene had almost no effect on the reaction. Bidiphenylene-ethylene and β-naphthoquinone were active antioxidants, but anthraquinone showed strong proöxygenic influence. Paraquinone had no effect and acenaphthenequinone almost none. Aldol-α-naphthylamine as well as an acetone extract of rubber had weak, and phenanthrenequinone or α-naphthoquinone strong polymerizing influence. The most highly colored compounds were the strongest antioxidants. Aldol-α-naphthylamine reduced slightly the polymerizing action of α-naphthoquinone.

When balata in solution was irradiated, rubrene and dehydrorubrene were distinct proöxygens, whereas bidiphenylene-ethylene and an acetone extract of rubber were without influence. Passage of the light through a toluene filter had no influence on its oxidizing action on balata or acetone-extracted rubber exposed to the air. All substances which acted as antioxidants when added to the rubber showed the same property when employed as external filters. Azobenzene and α-benzeneazo-β-naphthylamine also prevented autoxidation and α-naphthoquinone, phenanthrenequinone and alizarine retarded it greatly when their solutions were used as filters. A colored substance which absorbs active radiations inhibits autoxidation only if it is soluble in balata or acetone-extracted rubber. The antioxygenic power of an acetone extract of rubber depends in part upon its brown color, for even in very low concentrations, *e.g.*, 0.1 per cent in toluene as a light filter, it still retarded autoxidation. This does not mean, however, that the antioxygenic power depends only on the colored components. By means of filters, the spectral region which is active in autoxidation in sunlight was found to lie between 3000 and 4800A. In this ultraviolet region, the activity was apparently uniformly distributed. Sunlight and ultraviolet light were found to be similar in effects, in spite of the fact that ozone is formed only by the shorter wave-length ultraviolet light absent from sunlight.

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[64] See also van Rossem, A., and Talen, H. W., *Kautschuk*, 7, 79, 115 (1931); *Chem. Abs.*, 25, 5795 (1931).

[65] This could not be confirmed by van Rossem, A., and Talen, H. W., *Kautschuk*, 7, 79, 115 (1931); *Chem. Abs.*, 25, 5795-6 (1931).

[66] Bondy, H. F., and Lauer, G. G., *Ber.*, 66B, 1611 (1933).

[67] Bondy, H. F., *Rev. gen. caoutchouc*, 11, No. 1, 6, 9 (1934); *Chem. Abs.*, 29, 4207 (1935).

The rate of oxidation of vulcanized rubber in ultraviolet light and air or oxygen increases with the time of vulcanization. It is greatly increased by extraction with acetone. It varies greatly with the kind of rubber, vulcanized crepe oxidizing far more rapidly than vulcanized Para rubber, probably because ultraviolet light penetrates the former much more readily than the latter.[68] The difference in the rate of oxidation of unextracted and extracted vulcanized rubber is probably closely related to the condition of the sulfur and to the absorption of ultraviolet light, for it is known that ultraviolet light is completely absorbed by a vulcanized mixture which reflected it before vulcanization and that carbon disulfide containing sulfur absorbs ultraviolet light while carbon disulfide alone transmits it. This suggests a means of determining whether sulfur is chemically combined or in solution and suggests that chemical combination occurs during vulcanization. The primary yellow products of oxidation in ultraviolet light are converted by boiling dilute sulfuric acid to the same brown substances which are obtained on oxidation in darkness at 70°C. The immediate onset of oxidation in ultraviolet light is in contrast to the induction period in oxygen alone. The gain in weight occurring during the oxidation in ultraviolet light ceases long before the oxygen reaches the proportion represented by C_5H_8O. The rate of oxidation of vulcanized rubber in ultraviolet light and air at 40° to 45°C. is about three times that in air at 70°C. in darkness.

Kirchhof[69] later used the ability of the natural water extract of raw rubber to reduce an ammoniacal silver nitrate solution at room temperature in detecting the effect of light on rubber. After a brief exposure to light, crêpe still reduces the reagent with dispersion of silver throughout the rubber, whereas water-extracted crêpe or crêpe bleached with sodium bisulfite does not reduce the reagent. After prolonged exposure crêpe no longer reduces the reagent, because light in conjunction with oxygen destroys the reducing substances (probably sugars). There is also a bleaching effect, perhaps because of the formation of hydrogen peroxide. Ultraviolet light has the same effect as sunlight, except that there is a yellowing instead of a bleaching, perhaps because of peroxide formation.

In sunlight and ultraviolet light, purified gutta-percha slowly turns yellow and on treatment with ammonia-silver nitrate turns brown because of peroxide formation. Samples of pale crêpe with no reducing action were immersed in solutions of hydroquinone, phenyl-α-naphthylamine and the commercial antioxidants, Parazone ND and MB, dried in darkness, and exposed to ultraviolet light. There was no visible change except with the phenylnaphthylamine in which case yellowing occurred. On treatment with ammonia-silver nitrate, there was reduction with hydroquinone and Parazone, while with the phenyl-α-naphthylamine and Parazone MB, there was no reduction, even by the unexposed part. Since hydroquinone and Parazone have a marked protective action on rubber exposed to light, this action is related directly to the reducing power. The stability of hydroquinone and Parazone toward light accounts for the continued protective effect at low concentrations.

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[68] Kirchhof, F., *Kautschuk*, 239, 256 (1927); *Chem. Abs*, 21, 3766 (1927).

[69] Kirchhof, F., *Kautschuk*, 9, 70 (1933); *Chem. Abs.*, 27, 4126 (1933).

Dogadkin and Balandina[70] irradiated rubber with ultraviolet light under water in quartz flasks. Aqueous extracts were then prepared and tested for oxidation products which at 100°C. reduce gold salts to rose-colored colloidal gold. Unexposed pale crêpe and smoked sheet gave no reduction, but after ultraviolet irradiation they each reduced gold chloride. In each case on continued irradiation the concentration of colloidal gold increased to a maximum and then diminished. The electrical conductivity of the extracts, after diminishing slightly to a minimum after a certain period of irradiation, increased continuously.

Defries and Naunton[71] investigated the effect of sunlight on the color of cured and uncured accelerated mixes. Rubber mixtures containing crêpe 100, zinc oxide 10, barium sulfate 100, and sulfur and accelerator (diphenylguanidine, di-*o*-tolylguanidine, triphenylguanidine, mercaptobenzothiazole, thiocarbanilide, aldehyde-ammonia, tetramethylthiuramdisulfide and zinc diethyldithiocarbamate) were exposed to ultraviolet light. With all accelerators, exposure before curing gave no visible effect, but, when cured, the previously exposed samples were much darker than ones not so treated before curing. These darker samples could not be lightened by irradiation. Ultraviolet light induces oxidation of the vulcanizates. When the samples were undercured, a second exposure to light intensified the darkening. The results indicate, first, that exposure of uncured samples causes a surface vulcanization, second, the discoloration is an effect of a surface overcure produced by normal vulcanization superimposed on an already slightly vulcanized surface and third, bleaching of vulcanizates by light results from oxidation, since it can be minimized by exposure in an inert gas and can be produced by oxidizing agents. When, however, there is an excess of vulcanizing agent to permit after-vulcanization, a subsequent exposure induces further darkening instead of bleaching.

ACCELERATED WEATHERING TESTS

Artificial aging of vulcanized rubber was thought by Pelizzola[72] to be identical with natural aging, from both chemical and physico-mechanical points of view. Asano[73] directed experiments toward an understanding of the fundamental processes involved. As an aging test, he recommended that samples be maintained at 71°C. in a steady current of air and at the same time be exposed to ultraviolet light until the changes are of sufficient magnitude to compare the stress-strain curves and the chemical composition. By this test, rubber-insulated wire cracked after an hour, although it remained unchanged after fifteen hours in darkness.[74]

It must be noted that light is but one of several aging factors employed in accelerated aging tests, although it is the only one requiring mention here. Jecusco[75] placed a Uviarc in the accelerating cabinet 7 cm. above the reel which held the samples of rubber so that its rays fell at right angles to the narrow part of dumbbell samples held by clips. The oven was of a standard construction 3 feet deep, 5 feet high and 4 feet wide, with walls filled with 2-inch asbestos and air insulation. It had a specially constructed wooden reel, 24 inches in diameter and 28 inches long, having eight arms and eleven wooden cross rods one inch in diameter forming an open reel of the squirrel-cage type. This revolved on a shaft at 26 r.p.m. Underneath a perforated floor plate were enough electric heating units to give a temperature of 50 to 100°C., automatically controlled by a thermostat. Underneath the floor plates on either side of the oven were large adjustable air shutters and baffle plates to admit the circulation of air through the heaters. There was also a top vent with damper control.

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[70] Dogadkin, B., and Balandina, V., *Kautchuk*, **9**, 146 (1933); *Rubber Chem. Tech.*, **7**, 18 (1934); *Chem Abs.*, **28**, 4936 (1934).

[71] Defries, R., and Naunton, W. J. S., *Trans. Inst. Rubber Ind.*, **4**, 298 (1928); *Chem. Abs.*, **23**, 2068 (1929).

[72] Pelizzola, C., *Giorn. chim. ind. applicata*, **4**, 458 (1922); *Chem. Abs.*, **17**, 1559 (1923).

[73] Asano, K., *India-Rubber J.*, **70**, 307, 347, 389 (1925); *Chem. Abs.*, **19**, 3616 (1925).

[74] Asano, K., *Mem. Kyoto Univ.*, No. 3, 267, 1926; *Gummi-Ztg.*, **41**, 1576; *Chem. Abs.*, **21**, 2398 (1927). For other early tests, see also Jacobs, S., *Caoutchouc & gutta-percha*, **25**, 14,110 (1928) and Krahl, M., *Kautschuk*, 159, 180 (**1927**); *Chem. Abs.*, **21**, 2816 (1927).

[75] Jecusco, F. P., *Ind. Eng. Chem.*, **18**, 420 (1926). Recent aging apparatus is described by Walter, P., *Rev. gén. caoutchouc*, **14**, No. 134, 26 (1937).

When both light and heat were used, a sample gave twice as much acetone-extract as after the heat test alone. In the heat test there was merely a pronounced darkening at the end of 144 hours, but with light and heat, the sample began to fog after three hours, a brownish tint began to appear at six hours, and after nine hours it was decidedly brown. After 21 hours the sample started to darken not unlike a sample heated alone for 144 hours. It gradually became darker up to 39 hours when it threw a purplish hue over the brown. This colored coating was insoluble in all common organic solvents and in caustic soda solution. Even after three hours, the surface was somewhat checked. This was pronounced at 39 hours. It began to crack at six hours. A decided stiffening became apparent at 18 hours and continued to the end of the test. The loss of weight was, however, decreased in this test.

Other rays than those shorter than the 2250A (found active by Asano, who used only raw rubber) were effective in the aging of vulcanized rubber. Even sunlight was effective. Sunlight appeared to act in spurts. At 90°F. the first spurt from the cold Uviarc starts at the beginning of irradiation and continues until the breaking stress has been reduced from the initial 2260 to 1575 lbs. per square inch (fifteen hours) after which the deterioration is slow. At higher temperatures the spurts are more frequent and the delays shorter. The cause of these delays in the aging may be the formation of a protective coating. From filter experiments, it was concluded that green rays which have apparently no action on fresh rubber, have a tremendous effect on oven-aged rubber. Infrared rays showed an effect on both fresh and "activated" rubber. Apparently all rays have an action at some stage on the degradation of vulcanized rubber. The results seemed to indicate that light did not give a quantitative measure of the ability of rubber to withstand weathering.

Others, however, believed ultraviolet light to give a fair indication[76] of the ability of samples of raw or vulcanized rubber to withstand exposure to sunlight under natural conditions. The visible changes of individual samples are only relative and an adequate judgment of their aging properties requires the simultaneous exposure of samples of known aging properties. The ultraviolet light test is also useful in predicting the behavior of dyes in rubber.

Krahl[77] found ozonized air to have little effect on sharply bent rubber mixtures unless they were simultaneously exposed to ultraviolet light. Then they soon cracked at the bent sections. The resistance to such attack varies with different mixtures. In general, dark-colored mixtures crack sooner than light-colored ones, and overcured mixtures crack sooner than normally cured ones. In the aging test, Krahl exposed the samples intermittently to ultraviolet light so that their temperature did not rise to a point at which thermal changes become significant. He accomplished this by using a water-cooled rotating drum on which the radiation falls over one longitudinal section. The friction strength of insulating tapes in this test[78] first increased with the time of exposure and then decreased progressively until it was but negligible. In comparative tests in which the samples were merely heated in air at 70°C., the strength decreased progressively from the beginning.

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[76] K. L., *Gummi-Ztg.*, **41**, 417 (1926); *Chem. Abs.*, **21**, 510 (1927).

[77] Krahl, M., *Kautschuk*, 159, 180 (1927); *Chem. Abs.*, **21**, 2816 (1927).

More complicated tests have been devised. In one,[79] during each revolution of a wheel about eight feet in diameter, the samples were successively submitted to immersion in water, desiccation by a hot or cold air blast, ultraviolet radiations, ozone, etc.

Yamazaki[80] exposed samples of vulcanized rubber to sunlight filtered through one of four glass plates transparent to 2900, 3130, 3300 and 4360A, respectively. The effect of the unavoidable heating was studied in control experiments by air-heating at 70-71°F. in darkness for 150 hours. The color of vulcanized rubber became darker by air-heating, but when exposed to sunlight at 60-70°F. the change in color was far more remarkable. The higher the degree of vulcanization, the greater the change in color. Moreover, the rubber was hardened by the action of light. The shorter the wave-lengths and the higher the temperature, the sooner did hardening occur. The action of the rays of wave-length greater than 4300A was very weak except in the case of overvulcanized rubber which was noticeably hardened. The acetone extract increased with the time of exposure, the rate of increase being less the longer the wave-lengths used. In some cases, the acetone extract reached a maximum and then decreased. It was considered that the increase in acetone extract was due principally to the oxidation of the rubber. The subsequent decrease, when observed, was attributed to the conversion of a part of the oxidized product into substances insoluble in acetone. The action of light and heat also caused a remarkable decrease in the free sulfur. The time of vulcanization of rubber-sulfur mixtures had a marked effect on the aging properties.

The deterioration due to sunlight was great even in winter and was very marked in the spring at 60°F. The outer layers of test-pieces exposed to sunlight were quite brittle and inelastic but the inner layers were still fairly good. Test-pieces subjected to Geer oven tests showed but little difference between the outer and inner layers.

Differences between the effects of sunlight and a quartz mercury arc were noted by Weightman[81] in the case of vulcanized mixtures, particularly those which contained reclaimed rubber. Some samples of the latter which failed in service were comparatively resistant to ultraviolet rays. A violet carbon arc gave results more similar to those of sunlight. Temperature, humidity and air supply should be controlled during the test.

McKee and Depew[82] found that overcured mixtures become surface checked sooner than the corresponding undercured mixtures in the light test, although the reverse was the case in darkness. Paraffin and zinc oxide retarded this action of light.

The varied conditions under which rubber is used make it particularly difficult to find any one suitable artificial aging test. Bierer and Davis[83] believed that neither the Fade-Ometer (see Chapter 32) nor the ultraviolet light tests truly duplicate the effects of sunlight.

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[78] Krahl, M., *Gummi-Ztg.*, 42, 965 (1928); *Chem. Abs.*, 22, 1495 (1928).

[79] French office nationale des recherches et inventiones, *Rev. gen., caoutchouc*, No. 29, 11 (1927); *Chem. Abs.*, 21, 1899 (1927).

[80] Yamazaki, T., *J. Soc. Chem. Ind. Japan*, 30, 804 (1927); *Brit. Chem. Abs.*, B, 615 (1928); *J. Soc. Chem. Ind. Japan*, 31, 233, 243 (1928); *Chem. Abs.*, 22, 3066 (1928); Yamazaki, T., and Okuyama, K., *J. Soc. Chem. Ind. Japan*, 32, 367B (1929); *Brit. Chem. Abs.*, B, 250 (1930); *Caoutchouc & gutta-percha*, 27, 15,016 (1930).

[81] Weightman, H. E., *Rubber Age (N. Y.)*, 23, 75 (1928); *Chem. Abs.*, 22, 2290 (1928).

[82] McKee, R. H., and Depew, H. A., *Ind. Eng. Chem.*, 20, 484 (1928).

[83] Bierer, J. M., and Davis, C. C., *Ind. Eng. Chem.*, 21, 1008 (1929). See also Karpinsky, Z., *Przemysl Chem.*, 21, 202 (1937); *Chem. Abs.*, 31, 8989 (1937).

In the aging of rubberized balloon fabrics, according to Barr,[84] there are essential differences between the effects of ultraviolet light and of tropical sunlight. Losses in tensile strength of the fabrics were similar, but though the permeability of the samples exposed to ultraviolet light remained unaltered, those exposed to sunlight became extremely permeable and their sulfuric acid contents became relatively large. Ultraviolet light caused a disproportionately great deterioration of the cotton, whereas tropical sunlight acted relatively rapidly on the rubber and sulfur with the formation of sulfuric acid which in turn attacked the cotton. Organic dyes and inorganic pigments protect the cotton from sunlight, lead chromate giving the best results.

Graffe[85] finds that in the light test the increase in acetone extract and the gain in weight are parallel up to an advanced stage of deterioration, so that the progress of the aging can be followed by the gain in weight. By the use of intermittent exposures, it was found that at certain stages of the aging process ultraviolet light accelerates a subsequent autoxidation in the air.

Tanaka, Kambara and Fujita[86] state that the original cold elongation of vulcanized rubber is increased by exposure to ultraviolet rays.[87]

Ebonite that had been exposed under glass for fifteen years to light showed superficial cracking and masses of a whitish deposit.[88] The majority of samples showed a content of combined sulfur greater than that corresponding to the formula C_5H_8S. The exposure appeared to have caused oxidation of part of the caoutchouc to "resins," leaving a residue richer in sulfur. Certain of the samples containing organic softening ingredients such as palm pitch or carnauba wax had deteriorated less than the others.

Exposure of semi-ebonite to ultraviolet radiations[89] caused small increases in weight with the formation of a very thin hard and lustrous skin. Exposure outdoors also increased the weight and brought about surface changes. The effects of antioxidant both on exposure to ultraviolet rays and outdoors were relatively small.

Following an induction period, the electrical resistivity of the surface of low-grade loaded hard rubber and ebonite on exposure to light, air and humidity drops rapidly. It reaches a saturation point at about 10^7 to 10^8 ohms, after which it continues relatively slowly.[90] Ebonite, though initially superior to low-grade loaded hard rubber, deteriorated more rapidly and to a greater degree. After removal from the light, the resistivity of the low-grade loaded hard rubber increased slowly. The surface resistivity of ebonite was sensitive to the relative humidity during measurements, except during the induction and saturation stages. When the relative humidity during exposure was varied, there was found a maximum rate of deterioration of ebonite at 70-90 per cent relative humidity, indicating that both dry and saturated atmospheres had a retarding effect. In artificial light (15 cm. from a 100-watt gas lamp), deterioration was slower than in bright north light, but, in the case of ebonite, the results were the same when expressed in standard hours measured by a photographic exposure meter. The low-grade hard rubber deteriorated relatively less rapidly in artificial light, probably because of a recovery of its resistivity value. Accelerated and artificial light aging tests cannot yet be accepted as criteria of true relative stabilities in sunlight.

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[84] Barr, G., *Trans. Inst. Rubber Ind.*, **5**, 31 (1929); *Chem. Abs.*, **23**, 5350 (1929). Tests for rubber composition soles are described by Dock, E. H., *Trans. Inst. Rubber Ind.*, **13**, 160 (1937).

[85] Graffe, L., *Caoutchouc & gutta-percha*, **28**, 15,714, 15,797 (1931); *Chem. Abs.*, **26**, 622, 1152 (1932)

[86] Tanaka, Y., Kambara, S., and Fujita, H., *J. Soc. Chem. Ind. Japan*, **37**, 522 (1934); *Brit. Chem. Abs.*, **B**, 1071 (1934).

[87] For further general reviews of aging tests, see Garner, T. L., *Ind. Chemist*, **7**, 295 (1931); Moureu, C., Dufraisse, C., and Lotte, P., *Ind. Eng. Chem.*, **22**, 549 (1930); Jackson, H., *Trans. Inst. Rubber Ind.*, **10**, 292 (1934); *Chem. Abs.*, **29**, 3871 (1935); Carpenter, A. W., *India Rubber World*, **95**, No. 6, 39, 44, 48 (1937); Saito, S., *J. Soc. Rubber Ind. Japan*, **6**, 525 (1933).

[88] Scott, J. R., *Res. Assoc. British Rubber Mfrs.*, **5**, 2 (1936); *Brit. Chem. Abs*, **B**, 338 (1936).

[89] Gibbon, P. A., *Trans. Inst. Rubber Ind.*, **10**, 494 (1935); *Chem. Abs.*, **29**, 6468 (1935).

[90] Church, H. F., and Daynes, H. A., *J. Rubber Research*, **6**, 13 (1937); *Chem. Abs.*, **31**, 5211 (1937).

Turner[91] studied the influence on the sun-cracking of vulcanizates exerted by quantities of coloring matter too small to alter significantly the characteristics of the white base mixture. Inorganic and organic colors (both soluble and insoluble in rubber) including blue or black, red, green and yellow ones, were tested in two types of non-blooming white vulcanizate exposed under low stress (6 or 7 per cent elongation) to sunlight. In all cases, surface cracking took place much sooner when a coloring agent was present. Next to white vulcanizates, the blue ones were the slowest to crack. The resistance of the white vulcanizates was attributed to their ability to form a protective skin more readily than do the colored products. The coloring materials were thought to absorb wave-lengths which might otherwise be absorbed by the rubber and lead to the formation of the skin. A translucent vulcanizate absorbs more light than does a white one and therefore forms a protective skin more readily than does a corresponding opaque one. This was shown by the fact that a vulcanizate containing titanium dioxide cracked sooner than a corresponding one containing an equal volume of barium sulfate and having a more pronounced film. This may explain the beneficial effect of magnesium carbonate.

PROTECTION OF RUBBER

According to Schopper,[92] solutions of coumarin derivatives, *e.g.*, a 1-per cent solution of dimethylamino-methylcoumarin, may be used to absorb ultraviolet rays and protect the fabric of balloons from damage by sunlight. Jakowsky[93] calls attention to the opaqueness of the carbon black used as a reinforcing agent in rubber and notes the general belief that this property affords rubber of greater durability by preventing the penetration of light, especially ultraviolet rays, into rubber.

Shepard, Krall and Morris[94] attempted to determine the influence of various compounding ingredients, including fillers, softeners, accelerators, and an antioxidant, on sun-checking. They stretched the rubber to an elongation of 12.5 per cent and obtained checking of susceptible samples within 24 hours, although unstretched samples were not checked for months when exposed to sunlight. Dumbbell strips, 5 mm. thick, stretched on frames, were hung by ropes from the roof where they could revolve in the wind. It was concluded that, through the proper selection of rubbers, reclaim and compounding ingredients, it is possible to reduce to a marked extent the tendency of rubber products to check and crack. The maximum results from a checking standpoint would be obtained by using only those materials in compounding that are protective in their action. Unfortunately, however, selective pigmentation cannot usually be resorted to without the sacrifice of desirable physical properties. Carbon black, for example, has no protective action, and even in small quantities offsets the protective action of other pigments; but for tread stocks this pigment is highly desirable for toughness, resistance to tear and abrasion. Other characteristics, such as the blooming of certain protective materials, make their commercial application very difficult. There is little difference between the accelerators triphenylguanidine, diphenylguanidine and methylene-*p*-toluidine. Benzidine (the only antioxidant tested) has to be added to the extent of 3.6 per cent to give complete protection for a week. The solubility of a material in rubber plays a prominent part in its value as a protective agent. Mineral rubber and other asphaltic substances have no beneficial effect. Rosin and pine pitch are detrimental. Vegetable oils have little effect. Paraffin has a stronger protective action than Vaseline, but more than 2 per cent is necessary for complete protection. A light engine-oil is inferior to Vaseline. Crude Montan wax is but little if any better than asphaltic softeners. When refined, it is intermediate between Vaseline and paraffin. Zinc oxide and lithopone do not protect to the same extent as whiting and clay which are of low covering power. Low-grade off-color rubbers are not more susceptible to sun-checking than are high-grade rubbers. A white stock loses much more in resistance when made gray or black.

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[91] Turner, H., *Trans. Inst. Rubber Ind.*, **10**, 21 (1934); *Chem. Abs.*, **28**, 7591 (1934).

[92] Schopper, T., *Gummi-Ztg.*, **29**, 1250 (1915); *Z. angew. Chem.*, **28**, *Ref.* 644 (1915); *J. Soc. Chem. Ind.*, 356 (1916).

[93] Jakowsky, J. J., *Bureau of Mines Tech. Paper* 351 (1924); see also Bradshaw, H., *Ind. Eng. Chem.*, **19**, 1110 (1927).

[94] Shepard, N. A., Krall, S., and Morris, H. L., *Ind. Eng. Chem.*, **18**, 615 (1926).

Dyestuffs capable of absorbing ultraviolet light were added by Porritt and Dawson[95] who also used polyphenols and aminophenols as antioxidants. Lister found dragon's blood resin to offer no protection against oxidation in cured rubber proofing exposed to the weather and to ultraviolet light.[96]

Preservative paints or coatings for application to rubber goods may be made with a medium capable of swelling the rubber and a material, such as mineral rubber, to increase the viscosity and afford some mechanical protection. Small quantities of antioxidants, such as aldol-α-naphthylamine, and of yellow or red substances such as Oil Red S may be added.[97]

Henri[98] stated that litharge and antimony sulfide accelerate the changes produced by ultraviolet rays. Copper salts, even in traces, are bad,[99] while powdered glass, according to Ditmar,[100] protects in direct proportion to the amount present. Zinc oxide accelerates oxidation but not in any direct relation to its percentage

Kreusler and Budde[101] dipped vulcanized rubber articles into a paraffin bath at 100°C. to render them resistant to light and air. Himmelbauer and Co.[102] used Vaseline or ceresin wax. Ahrens[103] stated that in 1899 he added ceresin to a tread stock on the mixing mill and then exposed tires with half and half tread, one-half containing ceresin and the other not. The protective action observed in the presence of ceresin was ascribed to the chemically inert bloom or coating of ceresin. Chertoff[104] uses certain vegetable oils, including palm, rosin, pine and turpentine oils, with resins (dammar, rosin, copal), to prevent rapid deterioration and hardening of rubber with age. Paraffin, mineral and other non-drying oils have also been suggested by Repony.[105]

Mazurek and Josse[106] recommended that fabric for the Gordon Bennett Cup balloons be colored red or yellow to protect the mixture from light, and also that it be impregnated on both sides with Revertex mixture. Coe[107] combines chlorophyll green with rubber in such manner as to exclude all wave-lengths of light except those transmitted between 5270 and 6500A.[108]

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[95] Porritt, B. D., and Dawson, T. R., British P. 269,745, May 25, 1926, to Research Association of British Rubber and Tyre Manufacturers; *Chem. Abs.*, 22, 1498 (1928).

[96] Lister, W. N., *J. Soc. Chem. Ind.*, 46, 220T (1927); see also Kelly, A., Taylor, B. S., and Jones, W. N., *Ind. Eng. Chem.*, 20, 296 (1928).

[97] Poritt, B. D., Dawson, T. R., and Research Association of British Rubber and Tyre Mfrs. British P. 299,169. Sept. 29, 1927; *Brit. Chem. Abs.*, B, 937 (1928).

[98] Henri, V., *Caoutchouc & gutta-percha*, 7, 4372 (1910); Matter in this paragraph is derived from Shepard, N., Krall, S., and Morris, H.[94]

[99] Bing, K., *Kolloid-Z.*, 4, 232 (1909).

[100] Ditmar, R., *Gummi-Ztg.*, 21, 243 (1906).

[101] Kreusler and Budde, German P. 18,740, Aug. 26, 1881.

[102] Himmelbauer and Co., *Chem. Ztg.*, 36, 1441 (1912).

[103] Ahrens, F., *Chem. Ztg.*, 36, 1441 (1912).

[104] Chertoff, G. J., U. S. P. 1,379,743, May 31, 1921; *Chem. Abs.*, 15, 3414 (1921).

[105] Repony, D., *Rubber Age (N. Y.)*, 5, 5 (1919).

Bonding Rubber to Other Materials. Livings and Lacey[109] described a method of bonding unvulcanized rubber to metal, glass, or ebonite, by preparing a bonding surface on the rubber by exposure to ultraviolet rays. Rubber so treated may also be used to bond together materials of dissimilar or similar nature, such as metal and wood or metal and metal. The rubber is finally subjected to pressure and vulcanization.

In joining vulcanized rubber compositions to metals, glass, molded phenol condensation products, hard rubber, etc., Morse[110] inserts a sheet of rubber composition containing a vulcanizing agent such as sulfur, zinc oxide and glue. To reduce tackiness one surface of it is previously exposed to light from a carbon arc for a period sufficiently beyond that at which the tackiness of the rubber may be increased. It is inserted between the materials to be joined, with the unexposed surface of the sheet adjacent to the first-mentioned rubber composition and the sheet of rubber composition is vulcanized in place.

Chlorinated Rubber. In a patent for the production of plastic products from india-rubber, Dyche-Teague[111] states that rubber which has been thoroughly depolymerized by milling is dissolved in a suitable solvent (carbon tetrachloride or benzene) and then chlorinated. Additional depolymerization prior to chlorination may be effected by subjecting the solution to actinic light. Distillation removes the solvent and hydrogen chloride. The reaction product, which may contain 50 to 60 per cent of chlorine, forms fluid solutions which afford alkali- and acid-resistant lacquers or paints.

It has been said that chlorinated rubber prepared in the laboratory, besides being resistant to acids, alkalies, corrosive salts and strong oxidizing agents, is unaffected by ultraviolet light.[112]

In the preparation of chlorinated rubber[113] chlorine is introduced into solutions of rubber of a concentration of 2 per cent or less and of low viscosity, and the resulting rubber chloride solution is gradually poured into hot water in which is immersed a disintegrating apparatus whereby the solvent is evaporated and the chloride is reduced to the granular state. Prior to adding it to water, the solution may be reduced in viscosity by standing, exposure to light, or by the addition of alkali. The time for chlorination is also greatly reduced by irradiation.[114] Subsequent to chlorination, the product may be further irradiated (sunlight or mercury arc) until the desired viscosity is reached.

By the use of ultraviolet rays, Floresco[115] increases the concentration of rubber

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[106] Mazurek, S., and Josse, Z., *Przemysl Chem.*, **18**, 481 (1934); *Brit. Chem. Abs.*, **B**, 144 (1935).

[107] Coe, M. R., U. S. P. 2,042,333; *Chem. Abs.*, **30**, 5071 (1936).

[108] Note also for the effects of other light filters, Margaritov, V., *J. Rubber Ind. (U.S.S.R.)*, No. 1, 42, 1936.

[109] Livings, G., and Lacey, B., British P. 418,035, 1934, to Dunlop Rubber Co., Ltd.; Canadian Patent 354,930; *Chem. Abs.*, **29**, 2395 (1935).

[110] Morse, D. S., U. S. P. 2,047,880, July 14, 1936; *Chem. Abs.*, **30**. 6240 (1936).

[111] Dyche-Teague, F. C., British P. 305,968, Sept. 13, 1927; *Brit. Chem. Abs.*, **B**, 334 (1929).

[112] Kojima, K., and Toyabe, Y., *J. Soc. Chem. Ind. Japan*, **36**, 236B (1933); *Chem. Abs.*, **27**, 3852 (1933).

[113] British P. 400,898, Nov. 2, 1933, to Chemische Fabrik Buckau; *Chem. Abs.*, **28**, 2219 (1934).

[114] French P. 768,157, Aug. 1, 1934, to Chemische Fabrik Buckau; *Chem. Abs.*, **29**, 640 (1935); Mollney, E., German P. 660,524, May 28, 1938; *Chem. Abs.*, **32**, 6905 (1938).

[115] Floresco, N., French P. 768,632, Aug. 10, 1934; *Chem. Abs.*, **29**, 640 (1935); Floresco, N., and Pfrunder, N., French P. 787,212, Sept. 19, 1935.

solutions to be halogenated without increasing their viscosities. The rays were said also to activate the halogenation and increase the stability of the products formed.

Buisov, Molodenskiĭ and Mikhaĭlov [116] stated that a chlorinated rubber containing 51.1 per cent of chlorine did not disintegrate in ten hours of exposure to ultraviolet rays. A freshly prepared rubber solution which had been irradiated for six hours gave after fifty minutes of chlorination a product with 68.2 per cent of chlorine. On the other hand, a solution of rubber containing 10 per cent of benzoyl peroxide after irradiation for eight hours and chlorination for one hour gave a product containing only 40.2 per cent of chlorine. This was unstable to light and heat. They conclude that the rubber must be disaggregated but not oxidized if it is to yield a good chlorinated product.[117] In discussing the use of chlorinated rubber in lacquers, Rosenthal and Schulze [118] state that because of the action of ultraviolet rays upon this product, only pigmented films are of practical use. They recommend titanium dioxide, chromium trioxide green, iron oxide pigments and graphite. Among other substances proposed [119] to be added in amounts up to 5 per cent to increase the light-stability of chlorinated rubber are dicyclohexylamine, ditetrahydrofurfurylamine, methyleneaminoacetonitrile, cyclohexylamine-formaldehyde, cyclohexylamine acetonitrile, tetramethylthiuramdisulfide, diphenylguanidine and dihydroxydiphenylpropane. Campbell and Reed [120] find 4-hydroxy-2-methyl-N-phenylmorpholine the best of six new N-phenylmorpholines in protecting rubber from staining after artificial illumination. Baxter [121] finds that plasticizers absorbing wave-lengths shorter than 3100A, such as dibutyl phthalate, stabilize chlorinated rubber and protect it from discoloration by light. Ethylene oxide is also recommended by Becker.[122]

Ultraviolet light is used by Laurin and Bidot [123] in the preparation of a substitute for rubber. To a mixture of glue as hydrogel with gum tragacanth and wood dust there are successively added: glycerol, vegetable oils, such as castor or colza oil, a resinate treated with formaldehyde, a resin solution such as a solution of Bakelite in naphtha, potassium dichromate, and potassium alum. Each addition is followed by a homogenization and the mass is kept in darkness from the time the potassium alum is added for a variable time subsequently. Pieces of the product obtained are exposed to ultraviolet rays to effect stabilization.

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[116] Buisov, B. V., Molodenskiĭ, V. S., and Mikhaĭlov, N. I, *J. Rubber Ind. (U.S S.R.)*, **11**, 44 (1934); *Chem. Abs.*, **29**, 953 (1935).

[117] For the action of ultraviolet on chlorinated rubber, see also *Synthetic and Applied Finishes*, 65 (1934).

[118] Rosenthal, L., and Schulze, G., *Farben-Chem.*, **5**, 53 (1934); *Brit. Chem. Abs.*, **B**, 636 (1934).

[119] British P. 437,304, Oct. 22, 1935, to Wingfoot Corp.; *Chem. Abs.*, **30**, 2422 (1936). British P. 479,464, Feb. 7, 1938; *Chem. Abs.*, **32**, 5256 (1938).

[120] Campbell, A. W., and Reed, M. C., *Ind. Eng. Chem.*, **28**, 656 (1936).

[121] Baxter, J. P., *Chemistry and Industry*, 407 (1936); *Chem. Abs.*, **31**, 4531 (1937).

[122] Becker, W., *Rubber Tech. Conf., London, Preprint* No. **96**, May, 1938; *Chem. Abs.*, **32**, 8192 (1938).

[123] Laurin, L., and Bidot, E., U. S. P. 1,969,932, Aug. 14, 1934; *Chem. Abs.*, **28**, 6348 (1934).

Chapter 32

Textiles, Paper and Dyestuffs

Coarse yarns are less affected by light than are fine ones, because in the former the outer layers protect the inner strands.[1] Of the various fibers, Barr found silk to be more affected by light than cotton, but wool much less than either. Artificial silk is affected less than cotton.

Simola[2] found that exposure to sunlight through a double glass window for five warm months reduced the tensile strength of cotton 17.8 and of wool 7.3 per cent. The stretching properties were reduced an average of 12 per cent for cotton yarn and 37.7 per cent for worsted yarn. Fine-fibered wool suffered more than coarse-fibered.[2a]

Expressed as the hours of sunshine required to cause a loss of 50 per cent in tensile strength, the order of deterioration of various textile fibers is as follows: silk (200), jute (400), artificial silk (900), cotton (940), flax (990), hemp (1100), raw wool (1120), chromed wool (1900). In this evaluation, the varying thicknesses of the textiles were not taken into account.[3]

Moisture, contrary to previous opinions, favors the deterioration, especially in the case of wool and bast fibers. The purer the atmosphere, the less is the destruction.

Waentig[4] found the tearing strength of wool practically unaffected by sunlight or by rays from a quartz mercury lamp, the washed fibers being slightly more sensitive than the raw wool. Carver[5] recommended ultraviolet radiations for testing fabrics used in automobiles.

It has been proposed to increase the resistance of textiles to ultraviolet light and water[6] by subjecting them to the successive action of a tanning solution containing a wetting agent (5 per cent catechu and 5 per cent Tetraconite, a mixture of Turkey red oil, pyridine and tetrachloroethane), a mordanting solution (5 per cent lead acetate) and an oiling solution containing an aldehyde or ketone (5 per cent linseed oil in tetrahydronaphthalene with 2 per cent paraldehyde) to control the rate of oxidation during drying.

Cotton and Cellulose. Little is yet known as to the wave-lengths which are required for the destruction of cotton or cellulose. Barr[7] maintained it to be due chiefly to wave-lengths shorter than 4000A. Kauffmann[8] finds the region about 3500A probably effective, and states that visible light is without action.

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[1] Barr, G., *Trans. Faraday Soc.*, **30**, 284 (1924); Waentig, P., *Z. angew. Chem.*, **36**, 357 (1923).

[2] Simola, E. J., *Teknillinen Aikakauslehti*, **23**, 326 (1933); *Chem. Abs.*, **28**, 647 (1934), *Acta Fennica*, **6A**, 126 (1933).

[2a] Mercerized cotton lost 13.7 per cent in tensile strength and 27.3 per cent in elasticity.

[3] Sommer, H., *Chem. Ztg.*, **51**, 777 (1927). Later, with Heermann, P., *Leipzig Monats. Textilind.*, **40**, 207 (1925) the order is given as: mineral weighted silk, raw silk, jute, raw and bleached cotton, raw wool, mercerized cotton, nitro- and viscose rayons, chromed wool, bleached flax yarn, cuprammonium rayon, raw flax yarn.

[4] Waentig, P., *Z. angew. Chem.*, **36**, 357 (1923). See also *J. Soc. Chem. Ind.*, **39**, 512A (1920); Vignon, L., *Ibid.*, 482A; **42**, 825A (1923).

[5] Carver, W. L., *Automotive Industries*, May 8, 1011 (1924).

[6] British P. 263,102, Nov. 4, 1926, to Albert Meyer-Sans Boeuf Co.; *Brit. Chem. Abs.*, **1927B**, 746.

[7] Barr, G., *Trans. Faraday Soc.*, **20**, 284 (1924).

[8] Kauffmann, H., *Textilber.*, **7**, 617 (1926); *Chem. Abs.*, **20**, 3352 (1926).

Notwithstanding a considerable amount of work, the question as to whether an oxidation is involved cannot yet be said to have been definitely settled. Dyer and Dorée,[9] who reviewed some of the earlier observations, concluded that ultraviolet rays convert cellulose into oxycellulose with complete loss of tensile strength, a view shared by Barr,[10] and by Aston.[11]

A new point of view was introduced by Kauffmann,[12] who believed the deterioration to occur independently of the presence of oxygen and without any change in weight. He concluded that the recognized formation of oxycellulose is preceded by the production of a compound "photocellulose," the formation of which does not involve oxidation. Like oxycellulose, the "photocellulose" reduces silver salts or Fehling's solution and shows a yellow color with caustic soda and phenylhydrazine. It is soluble in sodium hydroxide solution and has the formula $C_6H_{10}O_5$.

The action of ultraviolet light during the sun bleaching of cotton leads to the production of "photocellulose," the formation of which can be followed by a method involving the use of potassium permanganate. In cotton fabrics exposed for 45 days, 1 to 2 per cent of "photocellulose" is produced. The observed increased affinity of the exposed cotton for methylene blue was not, however, ascribed by Kauffmann to the presence of "photocellulose." This view is accepted by Sommer.[13]

Barr and Hadfield,[14] however, concluded that an oxidation is involved. No significant change took place when strips of cotton cloth were exposed for six months to sunlight in sealed glass tubes containing hydrogen or about two-thirds saturated with water vapor. Similar exposure in tubes containing oxygen resulted in a considerable loss of strength, an increase in reducing power as shown by the copper number, and the production of carbon dioxide and carbon monoxide and perhaps hydrogen. The reaction was more rapid in the presence of moisture. There was a rough parallelism between the copper number and the quantity of carbon dioxide produced. With increase in the time of exposure, there was a continuous decrease in strength and of the viscosity of cuprammonium solutions prepared from the exposed cotton. The methylene blue absorption by the cotton showed first a fall and then a slow rise. In general, the modification of cotton produced by the light corresponded to that formed by mild oxidation with chlorine water. Cotton cloth previously steeped in 0.001*N* sulfuric acid is more highly reducing and shows a greater production of carbon dioxide under the same conditions of exposure. Precipitation of ferric hydroxide on the cotton before exposure results in an increased attack by the light, but lessens the formation of carbon dioxide.

These workers recognized, however, that at least two reactions may occur during the exposure of cotton to sunlight. Both are accompanied by a loss of strength and the development of reducing power. One reaction, however, produces much less carbon dioxide than the other, and is catalyzed by iron.

[9] Dyer, J., and Dorée, C., *J. Soc. Dyers Colourists,* 33, 17 (1917); *Chem. Abs.*, 11, 1753 (1917). See also Scheurer, A., *Bull. Soc. Mulhouse,* 80, 324 (1912). A recent review is given by Cady, W. H., *Am. Dyestuff Rept., 27 (Proc. Am. Assoc. Textile Chem. Colorists),* p. 325 (1938); *Chem. Abs.*, 32, 5632 (1938).

[10] Barr, G., *Trans. Faraday Soc.*, 20, 284 (1924).

[11] Aston, F. W., Report on the Action of Sunlight on Aeroplane Fabrics T1019, British Advisory Committee for Aeronautics, 1917.

[12] Kauffmann, H., *Textilber.*, 7, 617 (1926); *J. Soc. Chem. Ind.*, 817 (1926); *Chem. Abs.*, 20, 3352 (1926).

[13] Sommer, H., *Chem. Ztg.*, 51, 777 (1927).

[14] Barr, G., and Hadfield, I. H., *J. Textile Inst., Special Issue,* 18, 490 (1927); *Chem. Abs.*, 22, 2062 (1928).

The deterioration of linen also appeared to be the result of oxidation. Loss of strength occurred most rapidly in oxygen, less so in air, and was negligible in hydrogen, carbon dioxide or a vacuum.

According to Sharvin and Pakshver,[15] exposure of bleached, ether-extracted, washed and dried cotton in sealed tubes with oxygen to sunlight showed a simultaneous formation of oxycellulose, carbon dioxide and water. During the earlier part of the process, there seemed to be a definite relation between the amounts of carbon dioxide and of oxycellulose formed, although it could not be expressed stoichiometrically. Upon continued exposure, the carbon dioxide formation decreased, but the oxycellulose appeared to undergo a further oxidation. In addition to the formation of carbon dioxide and water, there were produced compounds which had the odor of furfural but did not give its reactions. The fabric lost both in strength and in weight.

Ditz [16] concludes that more work is necessary to explain the mechanism of the degradation of cellulose, an especially important reaction in the "grass-bleaching" of fabrics. Dumas [17] reviews the analytical methods employed in such investigations.

It has recently been noted [18] that the sorption of iodine from the vapor phase by cotton is greater after the cotton has been irradiated by ultraviolet light. Williams [19] observed that cotton or viscose yarns when deteriorated by excessive bleaching or ultraviolet irradiation, lose much of their remaining strength, when wet. The ratio between wet strength and air-dry strength appeared to be a function of the degree of deterioration.

When exposed to the quartz mercury-vapor lamp, cotton hairs lose strength at a constant rate until the tendering amounts to about 40 per cent; the rate then diminishes.[20] Over a small range, the rate of tendering is proportional to the intensity of the light. Cotton hairs of different origin exhibit specific differences in their susceptibility to light tendering. The proportional loss of strength of yarns is about half that of hairs fully exposed under the same conditions, the hairs in the yarns being tendered to the same extent as the yarns. Bleached cotton is more rapidly tendered than raw. Material dyed with chrome green is much more resistant than the undyed scoured material. Ferric hydroxide has a slight protective action. Cloth-dyed mineral khaki is as resistant as the chrome-dyed material, the effect being such as to extend the life of fabrics subject to strong illumination to as much as five or six times that of untreated materials. Organic dyes modify the rate of tendering of cotton by light, some favorably and others unfavorably, but the effect is never as large as that of chromium hydroxide.

Experiments conducted for the British Government indicated [21] that heavy cotton and linen tent fabrics are much less affected by sunlight than are the light and less exposed fabrics used in airplane and airship construction. Although such pigments as lead chromate diminish the deterioration by light, others, such as the stannates, tungstates and sulfides frequently used in fire proofing, accelerate it. Waterproofing frequently, but not always, has a beneficial action, depending on the process and materials used, the climatic conditions and the exposure.

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[15] Sharvin, V. V., and Pakshver, A., *Z. angew. Chem.*, **41**, 1159 (1928); *Chem. Abs.*, **23**, 3080 (1929).

[16] Ditz, H., *Z. angew. Chem.*, **40**, 1476 (1927).

[17] Dumas, M. J., *Rev. gen. mat. color.*, **41**, 149 (1937).

[18] Beutel, E., and Kutzelnigg, A., *Monatsh.*, **64**, 41 (1934); *Chem. Abs.*, **28**, 3591 (1934).

[19] Williams, J. G., *J. Soc. Dyers Colourists*, **48**, 167 (1932); *Chem. Abs.*, **26**, 4477 (1932).

[20] Cunliffe, P. W., Farrow, F. D., and Midgley, E., *J. Textile Inst.*, **19**, 169T (1928); *Brit. Chem. Abs.*, **B**, 563 (1928).

[21] Hunter, J. A., *Textile World*, **69**, 309, 315 (1926); *Chem. Abs.*, **20**, 827 (1926).

After 500 hours in sunlight, 35 white and dyed cotton fabrics tested by Grimes [22] showed losses in breaking strength of 18 to 49 per cent in the warp and 34 to 65 per cent in the filling. The mercerization of the Everfast suitings and broadcloths tested increased their resistance to tendering. In eight of fifteen dyed fabrics tested, less breaking strength was lost than in undyed fabrics. The time of exposure had far more effect on the loss of strength than had the temperature and relative humidity. Spectrophotometric analysis showed that sunlight affected the color of all white and dyed fabrics tested. The white ones became increasingly yellow with increased exposures.

The resistance of "tobacco cloth" to sun and rain may be improved by letting an acidulated solution of lead acetate penetrate it and then treating it with a solution of sodium dichromate so as to form lead chromate on the fibers.[23]

Anthracene yellow GC and Chrysoidine have been found unsatisfactory for the protection of cotton from deterioration by light.[24]

Cotton and viscose silk materials dyed with one of a large number of orange and yellow vat dyes (Indanthrene Yellow G and Alizanthrene Yellow 6R excepted) if exposed to light and air immediately after dyeing while the dye is in its leuco condition, become tendered by oxidation.[25] The dye itself may also be simultaneously oxidized, with consequent partial or complete decolorization. If a second dye is present (especially Ciba Blue 2B), this may be oxidized in preference to the cotton or the first dye. These effects also are produced when the dyed fabric is oxidized in darkness before exposure to sunlight or a Fade-Ometer, but are not produced if again washed before exposure. Tendering occurs if the washed fabric is further impregnated with a dilute solution of caustic soda containing sodium hyposulfite or hydrogen peroxide and then exposed to light and air By means of the starch iodide test it was shown that an active oxidizing agent, probably hydrogen peroxide, was formed during the oxidation of cotton dyed with Cibanone Yellow R. Certain direct dyes, including Diamine Fast Yellow and Chlorazol Fast Orange R, behave similarly to vat dyes in promoting tendering. The tendering of cotton when so exposed is rapid and may be serious in large-scale dyeing. For example, cotton fabrics lifted successively five times (ten minute exposure each time) from the dye liquor and exposed to light and air while being dyed with 20-per cent Cibanone Orange R had copper numbers of 0.2, (original fabric), 0.3, (dyed fabric not exposed), and 0.7, 1.3, 1.5, 1.7 and 1.75 (after five successive exposures). Viscose silk is particularly susceptible to tendering under these conditions. The destructive action of sunlight is not appreciably affected by transmission through plate glass a quarter of an inch thick or didymium glass opaque to yellow light.

A fading product of Ciba Blue 2B dyed on cotton, isolated by Scholefield, Hibbert and Patel,[26] appeared to be dibromoisatin. The fading products from cotton dyed with methylindigo gave the reactions of *o*-methylisatin. Hibbert [27] also impregnated calico, wool and cellulose acetate silks with 1,2,4-trihydroxyanthraquinone Purpurin. After 60 hours of exposure to the Fade-Ometer, a substance was extracted by carbon tetrachloride which was found to be a mixture of phthalic acid and phthalic anhydride. Impregnation of calico with phthalic acid and its anhydride followed by exposure to the Fade-Ometer and extraction with alcohol and carbon tetrachloride was found to increase its affinity for methylene blue. Tables showing the manner in which various dyes catalyze the tendering action of sunlight on cotton have been given by Vashist.[28]

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[22] Grimes, M. A., *Texas Agr. Sta., Bull.* 506, 5 (1935); *Chem. Abs.*, 30, 291 (1936).

[23] Rhodes, G. H., U. S. P. 2,026,190; *Chem. Abs.*, 30, 1247 (1936).

[24] Kauffmann, H., *Textileber*, 7, 617 (1926); *Brit Chem. Abs.*, 1926B, 817.

[25] Scholefield, F., and Patel, C. K., *J. Soc. Dyers Colourists*, 44, 268 (1928); *Brit. Chem. Abs.*, B, 811 (1928); *J. Soc. Dvers Colourists*, 45, 175 (1929); *Chem. Abs.*, 23, 4824 (1929).

[26] Scholefield, F., Hibbert, E., and Patel, C. K., *J. Soc. Dyers Colourists*, 44, 236 (1928); *Chem. Abs.*, 22, 3780 (1928).

[27] Hibbert, E., *J. Soc. Dyers Colourists*, 45, 204 (1929); *Chem. Abs.*, 23, 4824 (1929).

Haller and Wyszewianski[29] investigated the sensitization of the photodecomposition of cotton by a series of vat dyes by exposing 25 per cent[30] dyeings on 10 gm. of heavy cotton calico to sunlight at a 45° angle to the south under 2 mm. of Ultravit glass. The loss of tensile strength was 9 per cent in white bleached calico after 130 normal bleaching hours. When treated with various anthraquinone intermediates, the corresponding losses were: anthraquinone, 27 per cent; 2-methylanthraquinone, 46 per cent; 1-chloroanthraquinone, 32 per cent; 2-chloroanthraquinone, 41 per cent; 1-aminoanthraquinone, 17 per cent; 2-aminoanthraquinone, 18 per cent; anthraquinone-1-sulfonic acid, 13 per cent and anthraquinone-2-sulfonic acid, 20 per cent; anthraquinone-1,5-disulfonic acid, 24 per cent. Graphs showed a decrease of as much as 40 per cent in the tear strength of cotton dyed with certain anthraquinone dyes after only 79 normal bleach hours, the dyeings varying from 0.05 to 1.0 per cent. Henk[31] believes that in such cases the deterioration involves oxidation. It depends on the temperature, fiber structure and the presence of hydroxyl, amino or imino groups. The destructive process is hastened by such catalysts as the metal compounds in sizes and after-treatment, particularly chromium and copper salts, impure water containing manganese and nickel, and the titanium dioxide used in the manufacture of delustered rayons.

A method of producing light and elastic threads or cellulose cloths consists in impregnating them with the chlorates, bromates or iodates of metals of the second periodic group. These, under the influence of photoactive rays (but not ordinary light) degrade the fibers.[32]

Pacini[33] has made the claim that the tensile strength of cellulosic materials such as cotton may be actually increased by subjecting it to ultraviolet radiation controlled in a special manner to prevent the formation of detectable oxycellulose.[34]

Paper and Wood Pulp.[35] The bleaching of wood pulp, paper products or cotton textiles by chlorine is accelerated both by light and by increased temperatures. It is usually cheapest to depend upon the thermal reaction alone, but in certain cold climates where fuel is expensive, attempts have been made to employ artificially produced ultraviolet light for aiding the process. Escourrou[36] investigated the accelerating effect of a mercury-vapor lamp. Although the process could be carried out at a lower temperature, more chlorine was used, owing to the increased formation of chlorates which play no part in bleaching. Furthermore, the cellulose, as well as the non-cellulose impurities in the wood pulp paste, was attacked. The material thus obtained was rich in oxy- and hydro-cellulose, as shown by its enhanced copper number. The α-cellulose content fell and the β- and γ-cellulose content rose. Although this is not important in paper-making, it is a disadvantage when the material is to be employed for making viscose and certain kinds of cellulose nitrate. This effect is observed only when chlorine bleaching agents are used, but not with ozone or hydrogen peroxide. In knot-pulp, the use of ultraviolet light in conjunction with hypochlorite bleaching did not exert a deleterious action, presumably because the chlorine reacts more readily with the ligneous constituents than with cellulose.

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[28] Vashist, S. D., *Indian Textile J.*, **42**, 376 (1932); *Chem. Abs.*, **27**, 192 (1933).

[29] Haller, R., and Wyszewianski, L., *Melliand. Textilber.*, **17**, 45, 138, 217, 325 (1936); *Chem. Abs.*, **30**, 6566 (1936).

[30] Wahl, A., [*Rev. gen. mat. color.*, **38**, 217 (1934); *Chem. Abs.*, **28**, 4910 (1934)] links the destructive action of the dyes with an absorption band at about 3300 to 3700 A.

[31] Henk, H. J., *Monatschr. Textilind.*, **51**, 186 (1936); see also E. Baur, *Helv. Chim. Acta*, **20**, 879 (1937).

[32] French P. 803,145, Sept. 23, 1936, to Comptoir des textiles artificiel, *Chem. Abs.*, **31**, 2837 (1937).

[33] Pacini, A. J., U. S. P. 1,948,276, Feb. 20, 1934, to Millprint Products Corp.; *Brit. Chem. Abs.*, **B**, 1053 (1934).

[34] For the absorption of cellulose films in the extreme ultraviolet (800A.), see O'Bryan, H. M., *J. Opt. Soc. Am.*, **22**, 739 (1932). It has been shown that the change in absorption of alkali cellulose during xanthogenation may afford a method for following the progress of the process. Atsuki, K., and Sobue, H., *J. Soc. Chem. Ind. Japan*, **36**, Suppl. binding, 589 (1933); *Chem. Abs.*, **28**, 710 (1934).

[35] Data on the absorption spectrum of lignin have been given by Herzog, R., and Hilmer, A., *Ber.*, **64B**, 1288 (1931); *Papier Fabr. Tech. Wiss. Teil*, **30**, 205 (1932); **29**, 4-5; *Chem. Abs.*, **26**, 4309 (1932); Hilmer, A., *Ber.*, **66B**, 1600 (1933); Hägglund, E., and Klingstedt, F. W., *Z. physik. Chem.*, **152A**, 295 (1931); Stamm, A. J., Semb, J., and Harris, E., *J. Phys. Chem.*, **36**, 1574 (1932).

[36] Escourrou, R., *Chimie et industrie*, **19**, 989 (1928); *Brit. Chem. Abs.*, **B**, 168 (1929); *Pulp Paper Mag. Canada*, **26**, 1549 (1928); *Chem. Abs.*, **22**, 4791 (1928).

According to Edge and McKenzie,[37] light causes two changes in paper pulp, a yellowing and a fading or whitening. Sunlight causes a definite yellowing in three hours, and whitening only after about two weeks. The latter effect may be due to a bleaching of pulp constituents not removed in ordinary bleaching. Discoloration is more rapid at 90 per cent than at 30 per cent relative humidity, and is great for samples exposed to the sun's heat while shielded from its light. Yellowing by a mercury arc varies with the age of the lamp.

Wahlberg[38] believed illumination to effect a saving of bleaching liquor and of steam about equal to the cost of the light, but found application difficult because the light affects only the surface. Hirschkind, Pye and Thompson[39] obtain good results with a mercury arc, provided rays shorter than 3000A are removed since these are harmful to cellulose. Wave-lengths longer than 4000A are ineffective. The best range is 3500A[40] to 3850A.

Attempts at standardizing the test for the light-resistance of various fibrous paper-making materials have been made by Kovalevskii.[41] An ordinary carbon arc produced after 80 to 100 hours changes in the resistance to breaking of paper and fiberboard that were too slight to be of use in the rapid laboratory testing of these substances. However, a Sperry carbon arc (150 amps., 79 volts, 950,000 c.p.) gave satisfactory results in exposures of twenty hours at 1.3 meters, in the case of sheets from unbleached sulfite pulp, sulfate kraft, straw pulp, mechanical wood pulp, linen rags, cotton, spruce, jute and a mixture of 60 per cent wool and 40 per cent kraft. All materials showed a decrease of 15 to 59.5 per cent in the resistance to breaking, with unbleached sulfite the most and jute and the two straw stocks the least affected. This contradicted a prevalent idea of the excessive destructibility of materials derived from lignified fibers. The stretching power of raw materials was impaired, but to a lesser degree than the resistance to breaking. Mechanical wood pulp and wool showed an increase in the stretching ability. The tests showed that in the process of aging by heat and light, all grades of paper undergo an insignificant change in their tearing length, and that this factor is less characteristic of the physical changes than is the resistance to breaking. The sorption of anthracene oil on raw materials was but little affected, except that that of wood pulp and wool was slightly improved.

The reflection of ultraviolet light by paper is not very different from that of ordinary light.[42] Papers water- and oil-proofed by vinyl resins are more readily penetrated by ultraviolet light than ordinary paper.[43] When paper containing resins is exposed to the sun, it tends to become yellow and soluble in cold weak alkalies or water.[44] The results may differ when artificial ultraviolet light sources are employed and these should be used only in the absence of sunlight. Bleached and unbleached rosin darkens in light,[45] and ferrous resinates and rosin size, if contaminated with ferrous iron, are also light-sensitive. Ferric resinates, aluminum resinate and sodium resinate have no ability to cause yellowing of paper in light.

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[37] Edge, S. R. H., and McKenzie, H. M., *Proc. Tech. Sect. Paper Makers' Assoc. Gr. Brit., Ireland*, **17**, Pt. 2, 437 (1937); *Chem. Abs.*, **31**, 4113 (1937); Bakker, H., *Chem. Weekblad*, **34**, 543 (1937); *Chem. Abs.*, **32**, 3958 (1932).

[38] Wahlberg, H. E., *Ind. Pappers Tid.*, **38**, 481 (1934); *Chem. Abs.*, **28**, 7008 (1934).

[39] Hirschkind, W., Pye, D. J., and Thompson, E. G., *Paper Trade J.*, **105**, TAPPI Sect. 268 (1937); *Brit. Chem. Abs.*, **B**, 147 (1938).

[40] Hirschkind, W., Pye, D. J., and Thompson, E. G., *Paper Trade J.*, **105**, No. 18, 118 (1937); *Chem. Abs.*, **32**, 772 (1938).

[41] Kovalevskii, I. I., *Bumazhnaya Prom.*, 14, No. 2, 13 (1935); *Chem. Abs.*, **29**, 5264 (1935).

Oguri,[46] in giving data on the increase in the copper number of filter paper, tissue paper and viscose rayons which follows exposure of these products to the rays of a quartz mercury arc, attributed it to the action of ozone formed by the lamp. Aldehydes appeared to be formed even in the absence of oxygen. Bromley[47] noted that when pulp-sized paper of good quality and free from resin is irradiated by the mercury arc, it rapidly loses its property of ink resistance, and the surface color degrades to a brown shade. He believed the browning to be a function of the gelatin present, which he found to be degraded to simpler products.

Most studies of the deterioration of paper by light have been made in sunlight. Richter[48] found that after 50 to 100 hours, the sacrifice in tear strength and tensile strength was in general slight in comparison with the loss in folding endurance, even though the fold strength of the sample tested had been originally greatly enhanced by the application of glue. Rosin- and starch-sized papers were at least as sensitive to loss in writing qualities as were glue-sized papers. The protective effect of glass was marked in the case of papers made from purified wood fiber and sulfite papers were partly protected, but newsprint deteriorated as rapidly under glass as when exposed directly. When purified wood fiber papers under glass in hydrogen were exposed to sunlight, there was apparently no degradation. Sulfite papers under these conditions showed a loss in fold strength, although the copper number did not increase. When similar papers were exposed under glass with oxygen, they retained 78 and 38 per cent, respectively, of their original fold strengths. Changes in the copper number were in the same order. When air was substituted for oxygen, the fold strength retentions were 90 and 58 per cent, respectively. Neutral mineral oil coatings did not protect papers from oxidation in sunlight. A glycerolated paper was somewhat less sensitive. Surface sizing with various waxes and starch caused no improvement and rosin was definitely harmful. A coating of regenerated cellulose, prepared by means of properly applied viscose solutions, was advantageous both for fold strength and for fold retention. Sodium stannate appeared to have a protective action but deterioration was hastened by the presence of sodium molybdate or of iron compounds, at least in a water-leaf purified wood-fiber sheet. Water-leaf papers lose from one to two per cent in weight when exposed a hundred hours on each side. In wood veneer strips, the changes in copper number are very great and in the case of poplar wood a marked delignification takes place.

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[42] Déribéré, M., *Papier*, **38**, 1083 (1935); *Chem. Abs*, **30**, 2379 (1936).

[43] Ohl, F., *Wochlbl. Papier-Fabr.*, **67**, 5 (1936); *Chem. Abs.*, **30**, 2755 (1936); see also Chinchin, I., *Bumazhnia Prom.*, No. 12 (1924); 14, 12 (1935).

[44] Marini, M., *Bol. staz. sper. Carta*, **6**, 16 (1927); *Chem. Abs.*, **21**, 2188 (1927).

[45] Kimberly, A. E., and Hicks, J. F. G., *Bureau Standards J. Research*, **6**, 819 (1931).

[46] Oguri, S., *J. Soc. Chem. Ind. Japan*, **37**, 620B (1934); *Chem. Abs.*, **29**, 1241 (1935); for the effects of various surrounding oxygen concentrations, see Oguri, S., and Yamaguchi, T., *J. Soc. Chem. Ind. Japan*, **40**, 300B (1937). Oguri, S., and Takei, M., [*J. Soc. Chem. Ind.*, **41**, 3 (1938)] find only wave-lengths less than about 3640A effective.

[47] Bromley, H. A., *Analyst*, **58**, 29 (1933).

[48] Richter, G. A., *Ind. Eng. Chem.*, **27**, 177, 432 (1935).

Red, green, lemon-yellow, dark brown-yellow and light brown-yellow window glasses each afforded some protection when papers (double-sized rag, rosin-sized papers from 50 per cent rag and 50 per cent sulfite pulp and pure sulfite paper) were exposed to direct sunlight for 523 hours or to diffused sunlight for 767 hours. The degree of protection depended upon the extent to which the filters removed the shorter wave-lengths, the range between 4600 and 4000A being strongly injurious. The yellow, green, and red glasses afforded practically the same protection.[49] The brown-yellow glasses gave the least protection, since both of them transmitted some wave-lengths down to about 3300A.

Blaisdell and Minor[50] studied the aging properties of a very white facial tissue made of highly bleached wood fiber and of a cream-colored toweling of underbleached sulfite wood fiber, by determining the copper number and absorbent properties before and after exposure for one hour to a Victor ultraviolet lamp at a distance of ten inches at 38°C. The original copper numbers of papers of this type gave no clue as to their permanence. A large change in this test may be considered as indicative of a rapid loss of absorbent properties on normal aging.

A method advocated by Wright[51] for waterproofing paper consists in impregnating it with a solution of gelatin, casein, or similar protein, and bichromate of potassium or sodium. On exposure to the rays of a quartz mercury arc, the protein becomes insoluble and the paper is strengthened and made waterproof. The solution may also be added to paper pulp and the irradiation carried out after sheeting.

Ruderman[52] coats paper with a suspension of dry starch and sulfur in cold water and then exposes it to ultraviolet light.

Considerable application has been made of fluorescence in filtered ultraviolet light in the analysis of papers and paper-making materials but the discussion of this topic lies beyond the scope of this book.[53] Testi[54] states that with rays of 3000 to 4000A, sulfite cellulose yields a color not caused by lignin, sulfur or lignosulfurous materials, but by an unknown principle in wood and its bark which resists various chemical treatments. White papers containing cotton, linen and hemp fibers assume a light-yellow color, and paper from chemical cellulose a white color with slight yellow tinge, and paper prepared chiefly from mechanical wood pulp, an intense violet color.

In testing the water resistance of paper by a method of this type, Grant[55] grinds 100 gm. of icing sugar, dried at 100°C., in a mortar with 0.5 gm. of Rhodamine 6G and sprinkles it from a bottle through 70-mesh bronze gauze on the specimen (2 sq. in.) floated on distilled water at 21°C. The time is taken with a stop-watch until, in a dark room, the upper surface of the paper irradiated with filtered ultraviolet first exhibits a bright golden fluorescence. This means that the water has just penetrated the paper, causing solution of the dyestuff.

Artificial Silk. Grempe[56] states that in the weathering of rayon and silk fabrics, the destruction takes place on the surface exposed to the light. It is due to both water and the ultraviolet rays of the sun. These fabrics lasted for about half a year when exposed to the weather. Huezel[57] has given curves showing the effect of exposure to ultraviolet light on the strength of textile fabrics prepared from viscose. The damage to viscose rayon is slightly greater in an atmosphere of 45 per cent relative humidity than in one of 65 or 90 per cent.[58] Acetate rayon deteriorates less than natural silk or other types of rayons.[59] Among various protective agents tested, β-methylumbelliferone and tannic acid were the most effective when test pieces were exposed to daylight through 3 mm. of ordinary window glass for 250 hours. Other protective agents, Tannigen FC, zinc salicylate and maleic acid, were found better when the acetate rayon was exposed to daylight through Uviol glass. Quercitin was best when the samples were exposed to the light of a mercury arc. The protective agents were used in 2 per cent solution, 1 per cent being usually taken up by the fiber. Eichler gave the following results for the deterioration of various products. The first number is the percentage decrease in tensile strength resulting from six hours of exposure to the mercury vapor lamp and the second that after exposure of 250 hours to daylight through window glass; natural silk, 28, 62; cuprammonium rayon, 11, 57; viscose rayon, 4, 35; acetate rayon, 35, 24; acetate rayon dyed black, 0, 1.2; acetate rayon dyed blue, 11, 17; acetate rayon dyed brown, 11, 13; unbleached cotton, 0, 0.

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[49] Köhler, S., *Tek. Tid. Uppl. C Kemi,* **65,** 49 (1935); *Chem. Abs.,* **29,** 6379 (1935).

[50] Blaisdell, C. A., and Minor, J. E., *Paper Ind.,* **15,** 512 (1933); *Chem. Abs.,* **28,** 2525 (1934).

[51] Wright, W. L., U. S. P. 1,542,539, June 16, 1925; *Brit. Chem. Abs.,* **B,** 627 (1925).

[52] Ruderman, A., U. S. P. 1,723,581, Aug. 6, 1929; *Chem. Abs.,* **23,** 4573 (1929).

[53] For general discussions, see Déribéré, M., *Papier,* **38,** 637 (1935); *Chem. Abs.,* **29,** 7652 (1935); Grant, J., *World's Paper Trade Rev.,* **103,** 1463, 1506, 1508, 1550, 1588, 1666 (1935); *Chem. Abs.,* **29,** 5266 (1935); Lewis, S. J., *J. Soc. Chem. Ind.,* **41,** 99R (1922).

[54] Testi, G., *Raggi ultravioletti,* 297, 1926; *Chem. Abs.,* **22,** 1472 (1928).

[55] Grant, J., *J. Soc. Chem. Ind.,* **53,** 349T (1934); see also Noll, A., and Preiss, K., *Papier-Fabr.,* **35,** Tech. Tl., 213 (1937); *Chem. Abs.,* **31,** 7248 (1937).

[56] Grempe, P. M., *Kunst-Seide,* **9,** 462 (1927); *Chem. Abs.,* **22,** 2469 (1928).

[57] Huezel, P., *Rayon and Melliand Textile Monthly,* **16,** 161 (1935); *Chem. Abs.,* **29,** 3170 (1935).

In the preparation of a selvedge-resistant material, Malm and Fordyce[60] form a sheet containing an ester of cellulose having an unsaturated acyl group such as cellulose tricrotonate and polymerize it by intense ultraviolet light for about five hours, or heat it to 100°C. for at least 24 hours.

The solubility properties of organic derivatives of cellulose may be modified by treatment with ultraviolet rays in the absence of oxygen.[61]

Silk. The photochemical destruction of this fabric depends upon the pH at which the exposures are made.[62] The maximum stability to the light of a glass-enclosed carbon arc is at about pH 10, the pH being measured in the aqueous extract of the sample. Above pH 11 and below pH 3, the stability decreases rapidly. In the intervening range, a minimum exists in the neutral region, indicating that the protein salts formed with small quantities of acid or alkali are more stable than the pure protein.

During the deterioration of silk in sunlight or north skylight, the ammonia nitrogen content is increased, as a result of oxygen attacking the silk under the influence of light.[63] Saito[64] found that exposure of silk fabrics to direct sunlight for 49 days gave a loss of 95.3 per cent of their tensile strengths. Against this, coatings of antioxidants had little effect.

X-ray diagrams of unweighted silk appeared similar before and after exposure to an S-1 sunlamp, but photometric analysis indicated a decrease in fiber orientation, causing the long fiber arc to expand toward the character of a powder pattern.[65] Lead-weighted silk underwent the greatest deterioration.[66] Pure-dye and 25 per cent tin-weighted samples slightly increased in tensile strength when exposed to wave-lengths longer than 3400A, but 50 per cent tin-weighted silk showed little or no change under these rays. All samples showed the greatest deterioration when exposed to wave-lengths between 2600 and 3400A, or to the entire spectrum. In dyed silks, color fastness was not in general sufficient to withstand Kansas sunshine, although only one sample in thirteen faded by the Fade-Ometer test.[67]

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[58] Negishi, M., Umesawa, H., and Mori, H., *Rayon World*, **5**, No. 7, 1 (1937); *Chem. Abs.*, **32**, 4343 (1938).

[59] Eichler, A., *Melliand Textilber.*, **16**, 429 (1935); *Chem. Abs.*, **29**, 7084 (1935).

[60] Malm, C. J., and Fordyce, C. R., U. S. P. 1,973,493, Nov. 9, 1934, to Eastman Kodak Co.; *Brit. Chem. Abs.*, **B**, 737 (1935).

[61] Bincer, H., German P. 601,478, Aug. 16, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, **28**, 7527 (1934).

[62] Harris, M., and Jessup, D. A., *Bureau Standards J. Res.*, **7**, 1179 (1931); *Am. Dyestuff Reporter*, **20**, 795; **23**, 215 (1934). *Cf.* Trotman, S. R., *J. Soc. Chem. Ind.*, **55**, 325T (1936).

[63] Harris, M., *Textile Mfg.*, **60**, 420 (1934); *Chem. Abs.*, **29**, 4589 (1935); *J. Bur. Stands. J. Res.*, **13**, 151 (1934); *Am. Dyestuff Rept.*, **23**, 215 (1934); *Chem. Abs.*, **28**, 5675 (1934); Columbo, G., *Boll. ufficiale staz. sper. seta*, **4**, 73 (1934); *Chem. Abs.*, **31**, 8204 (1937).

[64] Saito, S., *J. Soc. Rubber Ind. Japan*, **7**, 92 (1934); *Chem. Abs.*, **28**, 3591 (1934).

[65] Bruner, E., and Goehring, M., *Textile Research*, **5**, 231 (1935); *Chem. Abs.*, **29**, 4948 (1935).

[66] Hess, K., and Bruner, E., *Kansas Agr. Expt. Sta. Rept.*, 120 (1934); *Chem. Abs.*, **30**, 2765 (1936).

Sericin solutions are cleared and reduced in viscosity by ultraviolet light.[68]

Wool. Exposed wool no longer gives the von Allwörden reaction.[69] Meunier and Rey [70] observed that neutral wool develops a rose-violet color when treated with the vapor or solution of quinone, but a deep brown if previously exposed to sunlight or ultraviolet rays, the wool becoming more acid. This sharp difference may be utilized for the production of photographic prints on woolen fabrics. The effect of the irradiation is not dependent upon the nature of the surrounding atmosphere.

The superficial erosion of woolen cloth exposed to the air is ascribed by Heermann to the action of ultraviolet rays (2000-3500A).[71] After exposure to sunlight, wool swells strongly in dilute alkali and crumples in a characteristic manner.[72] After such exposure, it is dyed more deeply by basic dyestuffs and less so by acid dyes. Those dyes which yielded darker shades on wool which had been affected by sunlight than on unexposed wool were called positive. Those which yielded lighter shades after exposure were called negative. The positive or negative behavior of a dye toward wool usually increased with the duration of the exposure of the wool, but after a direct exposure of about 300 hours which almost completely destroyed the epithelial scales of the wool, the effect diminished. Indigo is positive after the wool has been exposed 100 hours, but after 264 hours, it is strongly negative. The behavior of acid dyes on exposed wool varies according to the acidity or neutrality of the bath from which they are applied. Alizarin Cyanin Green G is negative when applied from a neutral bath or one containing 3 per cent of acetic acid, but is strongly positive when applied from a bath acidified with 2 per cent of sulfuric acid. The differences in the behavior of dyes toward exposed wool are very considerably diminished if the wool is chromed before dyeing. The intense yellow color of exposed wool dyed by immersion in a cold aqueous solution of methyl orange is not removed by washing with water. Under similar conditions the color is readily removed from non-exposed wool.

The interior of exposed wool is alkaline, since it gives a bluish-violet color with haematin. The outer part is acid and gives a yellow-brown color. After prolonged exposure to sunlight, the wool becomes brittle and the fibers may be easily broken. Exposed wool is much more easily wetted than unexposed wool.

Irradiated wool fails to give the usual colors when treated with ninhydrin or allantoin because of the presence of sulfur dioxide.[73] The increase in the content of labile sulfur is also shown by the reduction of nitro- compounds to amines. Insolation also increases the primary amino-groups as determined by the van Slyke method.

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[67] For further data obtained by the light of the carbon arc, see Appel, W. D., and Jessup, D. A., *Proc. Am. Assoc. Textile Chem. Colorists*, 350, 354, 1935; *J. Research Bureau Standards*, 15, 601 (1935).

[68] Kaneko, H., *Bull. Chem. Soc. Japan*, 9, 409 (1934); *Chem. Abs.*, 29, 662 (1935).

[69] Von Allwörden, K., *J. Soc. Chem. Ind.*, 35, 416 (1916); Naumann, K., *Ibid.*, 36, 707 (1917).

[70] Meunier, L., and Rey, G., *Rev. gen. mat. col.*, 28, 66 (1924); *J. Soc. Chem. Ind.*, 1924B, 370. *Compt. rend.*, 183, 596 (1926).

[71] Heermann, P., *Chem. Ztg.*, 48, 337 (1924).

[72] von Bergen, W., *Textilber.*, 6, 745 (1925); 7, 451 (1926); *Chem. Abs.*, 20, 2251 (1926); *Brit. Chem. Abs.*, B, 740 (1926).

[73] Meunier, L., and Rey, G., *Compt. rend.*, 183, 596 (1926); *Cuir Tech.*, 16, 530 (1927); *Chem. Abs.*, 22, 1047 (1928).

From 3.7 to 5.0 per cent of the sulfur content of cleaned wool samples is lost during exposure for 80 to 100 hours to the light from a quartz lamp.[74] This loss is more than doubled if the irradiation is followed by treatment with $0.001N$ sodium hydroxide. Microscopic examination shows the scales to be raised up; some are completely removed. It was suggested that the scales possess a higher sulfur content than the cortex so that a decrease in the number of scales explains in part the loss of the sulfur on irradiation.

Castiglioni [75] suggests that the yellowing of wool by ultraviolet light probably depends on the occurrence of the Salkowsky reaction between the sulfuric acid formed by oxidation of the sulfur of the wool and the cholesterol of the wool fat. Degreased wool tends to turn gray instead of the yellow to brown which forms in untreated wool.

The strength of wool is lost on exposure to light, slowly at first, then more rapidly and finally slowly again when but little strength is left.[76] Washing after exposure increases the loss of strength and results in a loss of weight owing to breakage of tendered surface hairs and to the dissolution of degradation products. Exposure also diminishes the extensibility. The product of extensibility and breaking load, a measure of the work of rupture, thus falls more rapidly than the breaking load itself and is probably a better measure of the useful strength of the cloth. The development of acidity is roughly parallel to the loss of strength. The Pauly test, however, gives positive results after a short exposure and soon reaches a maximum. Exposed cloth wets more rapidly and shrinks more when washed, but it fulls more slowly and has a lower regain.

Pretreatment of the wool with sulfuric acid is said to retard, and with alkalies to hasten, the deleterious action of light.[77] Rimington [78] has noted that free sulfhydryl groups are absent from normal wool and appear only after the action of alkalies or of ultraviolet light.

Smith and Harris [79] find irradiation of purified wool by the Fade-Ometer up to 100 hours progressively reduces its cystine content (from 12.2 to 7.9 per cent), with corresponding increases in ammonia nitrogen (0.28 to 1.22 mg. per gm.), alkali-solubility (11.9 to 36.2 per cent), and sulfate sulfur (0.06 to 0.37 per cent). Nearly all the sulfate sulfur in exposed wool is in the form of free sulfuric acid. There is a linear relation between cystine content and alkali-solubility in exposed wool. The deterioration is greater in wool previously treated by acid than in alkali-treated wool. The sulfur content of untreated and of acid-treated wool decreases during irradiation. This suggests that in the early stages, hydrogen sulfide is formed by a decomposition of the S—S group of cystine,[80] so that some is lost as hydrogen sulfide. The remainder is oxidized to sulfuric acid. Irradiation produces a type of oxidation different from that due to hydrogen peroxide. In nitrogen, hydrogen sulfide is evolved, the rate being increased by the presence of water.[81]

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[74] Barritt, J., and King, A. T., *J. Textile Inst.*, **20**, 151T (1929); *Brit. Chem. Abs.*, **B**, 846 (1929); see also Sommer, H., *Chem. Ztg.*, **51**, 777 (1927).

[75] Castiglioni, A., *Chim. e l'Ind.*, **17**, 82 (1935); *Brit. Chem. Abs.*, **B**, 540 (1935).

[76] Cunliffe, C. W., *J. Textile Inst.*, **27**, T25 (1936); *Chem. Abs.*, **30**, 3244 (1936).

[77] Sommer, H., *Chem. Ztg.*, **51**, 777 (1927). See, however, Smith and Harris.[79]

[78] Rimington, C., *Biochem. J.*, **24**, 205 (1930).

[79] Smith, A., and Harris, M., *Am. Dyestuff Reptr.*, **25**, 383P, 542P (1936); *Brit. Chem. Abs.*, **B**, 828 (1936); *J. Research Bureau Standards*, **17**, 97 (1936); *Rayon Textile Monthly*, **17**, 501, 727, 795 (1936).

[80] See also McMahon, P. R., and Speakman, J. P., *Trans. Faraday Soc.*, **33**, 844 (1937).

[81] Harris, M., and Smith, A. L., *J. Research Bureau of Standards*, **20**, 563 (1938).

In order to ascertain the likelihood of oils staining textile fabrics, Gray[82] proposes to expose pieces of tape, treated with the oil, to the light of a quartz mercury arc, using a standard oil for purposes of comparison. A half-hour exposure at a distance of six inches from the lamp was found sufficient to develop a stain with oils likely to discolor fabrics.

Paine, Radley and Rendell obtain fabrics fluorescent in ultraviolet light by impregnating them with an aminostilbenesulfonic acid.[83, 84]

Photochemistry of Dyes[85]

Diazo-Compounds and Azo Dyes. According to Eggert and Schröter,[86] nitrogen is evolved at a constant rate during the photochemical decomposition of the diazo- compounds derived from 2-amino-α-naphthol-4-sulfonic acid and *p*-aminodiphenylamine. This diminishes gradually when the illumination is withdrawn. The quantum yield (about 0.35) is independent of the intensity and wave-length of the light and of the temperature and concentration of the diazo-solution. The same quantum yield is obtained when the solid compounds are studied. Schröter[87] also determined the rate of fading by comparison with color standards. The quantum yields so determined were somewhat higher, the deviations being considerable in the case of the product from *p*-aminodiphenylamine. The lower values found by measurement of the evolution of nitrogen are attributed to the occurrence of side reactions which inhibit the complete evolution of the liberated nitrogen. On adding acid, the yield is unchanged in the case of 2-amino-α-naphthol-4-sulfonic acid, but acid reduces that of the *p*-aminodiphenylamine compound from 0.52 to 0.35. Alkali reduced the quantum yield of the former to 0.15. With the latter, precipitation occurred. In alcohol solution, the yield is increased to 0.5 to 0.6 for both substances, possibly because of the formation of a soluble diazo-molecule-alcohol complex which favors the reaction.

Schmidt and Maier[88] concluded that the bleaching of 1,2,4-diazonaphtholsulfonic acid (long used in the preparation of light-sensitive papers) in acid solutions exposed to direct sunlight, proceeds quantitatively with evolution of nitrogen and replacement of the diazo- group by a phenol radical. The reaction was conducted in acid solution so that the disturbing formation of azo dye in the bleached solution could not take place. Fukushima and Horio [89] find the reaction due to rays shorter than 4500A, the photolysis being a reaction of zero order. It is not affected by change of temperature. The quantum yield was 0.16 at 3666A. The addition of salts [90] had no effect on the order of the reaction.

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[82] Gray, T. T., *Oil Paint and Drug Reporter*, Aug. 9, 1915.

[83] Paine, C., Radley, J. A., and Rendell, L P, U. S. P. 2,089,413, Aug 10, 1937, *Chem. Abs.*, **31**, 7264 (1937).

[84] For fluorescence tests applied to various textiles, see Derrett-Smith, D. A., *J. Textile Inst.*, **28**, T145 (1937); *Chem. Abs.*, **31**, 7256 (1937); Korda, P., and Déribéré, M., *Tech. moderne*, **29**, 355 (1937); Henk, H. J., *Kunstseide und Zellwolle*, **19**, 426 (1937); *Chem. Abs.*, **32**, 3620 (1938); Radley, J. A., *Analyst*, **63**, 266 (1938); *Chem. Abs*, **32**, 4344 (1938); Tupholme, C. H. S., *Textile Colorist*, **60**, 441 (1938); Radley, J. A., *J. Soc. Dyers Colourists*, **53**, 376 (1937); Whittaker, C. M., *J. Soc. Dyers Colourists*, **53**, 468 (1937); *Chem. Abs.*, **32**, 1461 (1938). Undyed wool shows a weak violet fluorescence and undyed casein fiber a dead-white one. The results of ultraviolet-lamp readings should be considered as presumptive only, and should be rejected in the presence of contradictory evidence.

[85] For absorption data and a discussion of chromophore theories, see Brode, W. R., *Ber.*, **61B**, 1722 (1928); *Bureau Standards J. Research*, **2**, 501 (1929); *J. Am. Chem Soc.*, **48**, 1984 (1926); **51**, 1204 (1929); Obreimov, I. V., and de Haas, W. J., *Proc. K. Akad. Wetensch. Amsterdam*, **32**, 1324 (1929); Blumberger, J. S. P., *Chem. Weekblad*, **25**, 282, 315 (1928); **29**, 454 (1932); **30**, 538 (1933); **32**, 6, (1935); Hodgson, H. H., and Rosenberg, W., *J. Soc. Chem. Ind.*, **49**, 405T (1930); Szegö, L., *Ber.*, **61B**, 2087 (1928); **62B**, 736 (1929); Cambi, L., and Szegö, L., *Ber.*, **61B**, 2081 (1928); Funkhouser, J., and Brode, W., *J. Am. Chem. Soc.*, **56**, 2172 (1934); Piper, J., and Brode, W., *J. Am. Chem. Soc.*, **57**, 135 (1935); Chakravarti, G. C., *J. Indian Chem. Soc.*, **8**, 503 (1931); Mangini, A., *Gazz. chim. ital.*, **65**, 298, 308 (1935); Barkoff, S., *Bull. soc. chim.*, **2**, 1288 (1935); Foster, D. G., *J Am. Chem. Soc.*, **53**, 654 (1931); Maki, T., *J. Soc. Chem Ind. Japan*, **34**, 496 (1931); Luszcak, A , and Grün, L., *Monatsh.*, **64**, 349 (1934); Griffith, M. E., and Brode, W. R., *Ohio Agr. Expt. Sta., Bimonthly Bull.*, **192**, 122 (1938); *Chem. Abs.*, **32**, 7732 (1938); Lazarev, P., *Chimie et Industrie*, Special No., 457 (1928); Schumm, O., "Die spektrochemische Analyse natürlicher organischen Farbstoffe," Jena, Fischer; Zintl, E., and Rauch, A., *Ber.*, **58B**, 234 (1925); Hirschler, L., *Biochem. Z.*, **190**, 411 (1927); Szilard, A., *Ibid.*, **170**, 185 (1926); Speas, W., *Phys. Rev.*, **31**, 569 (1928); Merritt, E , *Ibid.*, **28**, 684 (1926); Prideaux, E., *J. Soc. Chem. Ind.*, **45**, 664, 678, 697 (1926); Dutt, S., *Quart. J. Indian Chem. Soc.*, **4**, 99 (1927); Holmes, W., and Peterson, A., *J. Phys. Chem.*, **36**, 633 (1932); Hewitt, J., *Sci. J. Roy. Coll. Sci.*, **3**, 27 (1933); Scheibe, G., *Kolloid-Z.*, **82**, 1 (1938); Scheibe, G., and Kandler, L., *Naturwiss.*, **26**, 412 (1938); Sen-Gupta, S. B., *J. Indian Chem. Soc.*, **15**, 263 (1938); *Chem. Abs.*, **32**, 8939 (1938).

[86] Eggert, J., and Schröter, W., *Z. Elektrochem.*, **34**, 602 (1928).

[87] Schröter, W., *Z. wiss. Phot.*, **28**, 1 (1930); *Chem. Abs.*, **25**, 43 (1931).

[88] Schmidt, J., and Maier, W., *Ber.*, **64B**, 767, 778 (1931).

Horio [91] exposed papers treated with a series of diazo- compounds in a spectrograph to the mercury and tungsten arcs and found their spectral sensitivities to be simply related to their extinction coefficients, at least in the case of copying papers of 1-diazo-β-naphthol-4-sulfonic acid and of *p*-diazo-diphenylamine sulfate. In an extension of this work [92] in which various diazo- compounds on paper were similarly exposed to an iron arc, and developed with suitable azo- compounds, it was found that some benzenediazonium compounds were decomposed at wave-lengths less than 4000A, independently of the position of the substituent. The threshold values for light-sensitiveness coincide well with the limits of the molecular absorption.[93] Yamamoto [94] determined the effect of sunlight upon the rate of decomposition of α-naphthalene diazonium chloride. The velocity constant became twenty times greater in clear weather, 2.7 to 11 times greater when there was slight cloudiness, and was not increased in completely cloudy weather.

Crystal Scarlet is visibly oxidized and reduced when no special depolarizer is used in the presence of zinc oxide as photosensitizer.[95]

Ultraviolet light causes a gradual fading of 0.005 per cent Congo red, the reaction not being due to ozone.[96]

The photochemical reduction of methyl red in methanol by phenylhydrazine with chlorophyll solution as a photosensitizer by the wave-length 4358A is zero molecular in order, according to Ghosh and Sen-Gupta.[97] Its velocity is independent of the phenylhydrazine concentration and of temperature (25 to 35°C.) and reaches a maximum at a 5×10^{-5} molar concentration of chlorophyll. The quantum efficiency is 0.45 when only the radiation absorbed by the chlorophyll is considered. The dark reaction is extremely slow. In benzene, however, the reaction is unimolecular with a constant proportional to the phenylhydrazine concentration and a quantum yield of 0 05. For the wave-length 5460A, the reaction in both methanol and benzene is zero-molecular with a velocity independent of the phenylhydrazine concentration. The quantum yield varies between 1.0 and 0.1, decreasing with increasing chlorophyll concentration. If phenylhydrazine hydrochloride is used, the dark reaction has a measurable speed, independent of the chlorophyll concentration. The light reaction has a very low quantum yield and small temperature coefficient. Its unimolecular constant is proportional to the concentration of the reducing salt. An activated complex of chlorophyll and methyl red is believed to play a part in the reaction mechanism.

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[89] Fukushima, I., and Horio, M., *J. Soc Chem. Ind. Japan*, **34**, 372, 374 (1931); *Chem. Abs.*, **26**, 2377 (1932); *Mem. Coll. Eng. Kyoto Imp. Univ.*, **6**, 179 (1931); *Chem. Abs.*, **25**, 4797 (1931).

[90] Kogan, N. M., Pischulina, A. F., and Ankinovich, A. G., *Anilinokrasochnaya Prom.*, **2**, No. 11, 34 (1932); *Chem. Abs.*, **27**, 5321 (1933).

[91] Horio, M., *Mem. Coll. Eng. Kyoto Imp. Univ.*, **8**, No. 1, 26 (1934); *Chem. Abs.*, **28**, 5338 (1934).

[92] Horio, M., *J. Soc. Chem. Ind. Japan*, **37**, 322 (1934); *Chem. Abs.*, **28**, 6637 (1934).

[93] The results have also been extended to solutions containing, in addition to the diazo- compound, varying amounts of Crystal Scarlet 6RA Extra and of Orange II. Horio, M., and Yamashita, S., *Z. wiss. Phot.*, **33**, 273 (1935); *Brit. Chem. Abs.*, **A**, 713 (1935).

[94] Yamamoto, E., *J. Soc. Chem. Ind Japan*, **38**, 275B (1935); *Chem. Abs.*, **29**, 6492 (1935).

[95] Fukushima, I., Horio, M., and Ohmori, M., *J. Soc. Chem. Ind. Japan.*, **35**, 398B (1932); *Chem. Abs.*, **26**, 5848 (1932).

[96] Puchkovskii, B. S., and Nekludov, V. N., *Kolloid-Z.*, **66**, 191 (1934); *Chem. Abs.*, **28**, 2623 (1934).

[97] Ghosh, J. C., and Sen-Gupta, S. B., *J. Indian Chem. Soc.*, **11**, 65 (1934); *Chem. Abs.*, **28**, 3662 (1934).

Since the photolytic oxidation of cellulose is accompanied by the evolution of carbon dioxide and since cotton dyed with simple azo-dyes yields more carbon dioxide upon irradiation than undyed cotton, Haller and Ziersch [98] conclude the dye fading to be an oxidative process. The carbon dioxide production is greater when the samples are exposed in an atmosphere rich in oxygen.

Exposure of a dilute (1 : 10,000) aqueous solution of 1-*p*-sulfobenzeneazo-N-phenyl-β-naphthylamine to sunlight gives *ang.* naphtho-phenazine and mainly the betaine of 3-phenyl-2-*p*-sulfophenyl-$\alpha\beta$-naphth-1,2,3-triazolium hydroxide.[99] Exposure of 1-benzeneazo-N-phenyl-β-naphthylamine on cotton immersed in water gives after concentration of the extract and treatment with picric acid, 2,3,-diphenyl-$\alpha\beta$-naphth-1,2,3-triazolium picrate, but not *ang.* naphtho-phenazine. The N-benzyl derivative of 1-benzeneazo-N-phenyl-β-naphthylamine is much more stable to light. Diphenyl-4,4-*bis*-(8-azo-N-phenyl-β-naphthylamine) on cotton is bleached rapidly by sunlight in air or oxygen. In nitrogen, bleaching is very slow. Azo- dyes from N-alkyl-β-naphthylamines are not so readily convertible into triazolium salts and are much more stable in light.

Golden yellow solutions of $(C_6H_5)_3CN{=}NC_6H_5$ are decolorized rapidly when exposed to light of short wave-lengths.[100]

Triphenylmethyl and Triphenylmethane Dyes. The free radical, triphenylmethyl, was found by Gomberg and Cone [101] to be bleached in sunlight in benzene solution with the production of triphenylmethane and unidentified substances. Schmidlin and Garcia-Banús [102] and, more recently, Bowden and Jones [103] found the products to be triphenylmethane and diphenyl-*bis*-diphenylenethane. The process occurs slowly in diffused light. Visible light (5300-4000A) is the most active portion of the spectrum. The presence of triphenyl peroxide or triphenylchloromethane does not alter the reaction, but the nature of the solvent has a marked effect on the rate of the reaction. In toluene, decolorization was more rapid than in benzene; in 1,3,5-trimethylbenzene and *m*-xylene it was even faster, and in hexane, the most rapid. No loss of color was observed in sulfur dioxide solutions and in the solid state the photochemical change was of a low order.

Triphenylmethyl peroxide has been obtained in 45 per cent yield by exposing a cyclohexane solution of triphenylbromomethane with air or oxygen for eight days to light (less than 3800A) from a Pyrex mercury arc.[104] It is highly probable that triphenylmethyl and bromine are formed by primary dissociation.

According to Tănăsescu,[105] 2,4-dinitrotriphenylmethane on insolation in neutral solutions yields the red O-quinone derivative, and in pyridine, the green nitrosocarbinol. In sunlight, 5-chloro-2-nitro-4′,4″-diaminotriphenylmethane gives [106] a blue compound and a compound $C_{38}H_{30}O_2N_6Cl_2$, reduced by tin and hydrochloric acid to 2,4,′4″-triaminotriphenylmethane. Similarly, 2-nitro-4′,4″-diaminotriphenylmethane gives a blue compound and a compound $C_{38}H_{32}O_2N_6$. The diethylmercaptol of Michler's ketone [107] quickly turns green in light, especially when moist. A solution of triphenylmethane and triphenylchloromethane in light forms triphenylmethyl reversibly.[108]

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[98] Haller, R., and Ziersch, G., *Melliand Textilber.*, 10, 951 (1929); *Chem. Abs.*, 24, 3373 (1930).

[99] Krollpfeiffer, F., Mühlhausen, C., and Wolf, G., *Annalen*, 508, 39 (1933); see also Witt, O. N., *Ber.*, 20, 571 (1887).

[100] Lifschitz, I., *Ber.*, 58B, 2434 (1925).

[101] Gomberg, M., and Cone, L. H., *Ber.*, 37, 3545 (1904).

[102] Schmidlin, J., and Garcia-Banús, A., *Ber.*, 45, 1344 (1912).

[103] Bowden, S. T., and Jones, W. J., *J. Chem. Soc.*, 1149 (1928).

[104] Halford, J. O., and Anderson, L. C., *Proc. Nat. Acad. Sci.*, 19, 759 (1933).

[105] Tănăsescu, I., *Bull. soc. chim.*, 39, 1718 (1926); see also *Chem. Abs.*, 21, 533 (1927) for *o*-nitrotriphenylmethane.

[106] Tănăsescu, I., and Suciu, M., *Bull. soc. chim.*, 4, 245 (1937); *Brit. Chem. Abs.*, A II, 375 (1937).

[107] Madelung, W., *J. prakt. Chem.*, 114, 1 (1926).

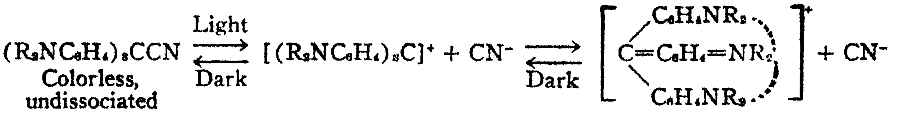
[108] Schlenk, W., and Herzenstein, A., *Ber.*, 43, 3545 (1910).

$$(C_6H_5)_3C.Cl + (C_6H_5)_3CH \longrightarrow HCl + 2(C_6H_5)_3C$$

It has long been known[109] that the leucobases of triphenylmethane dyes (brilliant green, malachite green, crystal violet, etc.) are highly light-sensitive, readily producing the corresponding dyes. König[110] made some attempts to utilize these photoöxidations in color photography. Eder[111] believed that, mixed with collodion, the leucobases form films more light-sensitive than the dyed silver halide films previously used in the photometry of the visible region. Carroll[112] found these reactions to show no induction periods and to be proportional to the light intensity. The sensitivity was, however, too low for practical photographic application, although the oxidations may be accelerated by nitrogen bases, as heterocyclic and aliphatic amines.

Little use has been made of this behavior in actinometry. An important application of crystal violet and, particularly, malachite green in actinometry is, however, based upon a reaction of their leucocyanides, originally described by Lifschitz.[113] It had been known that the addition of potassium cyanide to a triphenylmethane dye bleaches it with the production of a colorless triarylacetonitrile. Lifschitz showed that the colorless alcoholic solutions of the latter products were rapidly converted into the corresponding dyes when irradiated by an iron-nickel arc. The change occurred but slowly in sunlight in glass, so that it is due to the ultraviolet rays. When placed in darkness, the dyes again lose their colors. The leucocyanides in alcohol were not electrolytes. Irradiation was believed to convert them into colored, dissociated dye ions and cyanide ions, since the conductivity could be shown to increase. It was possible to demonstrate the liberation of the cyanide ion by setting up concentration cells of dark and illuminated solutions with silver cyanide coated electrodes.

Similar behavior was encountered in the thiocyanates and sulfonates of the triphenylmethane dyes, as well as in the dihydroxy-derivatives (benzaurin) and in unsubstituted triphenylmethyl cyanide. It became apparent that triphenylmethane derivatives can exist both in non-electrolyte and electrolyte forms. The primary photochemical effect was believed to consist in the transfer of a valence electron from the carbon atom to the cyanide or other group, which thereby becomes an ion. The triphenylmethyl ion need not, however, be colored until after it has undergone a further constitutional alteration. Lifschitz represented the process as follows:



$$\underset{\text{Colorless, undissociated}}{(R_2NC_6H_4)_3CCN} \underset{\text{Dark}}{\overset{\text{Light}}{\rightleftarrows}} [(R_2NC_6H_4)_3C]^+ + CN^- \underset{\text{Dark}}{\rightleftarrows} \left[C \begin{matrix} \diagup C_6H_4NR_2 \\ =C_6H_4=NR_2 \\ \diagdown C_6H_4NR_2 \end{matrix} \right]^+ + CN^-$$

Harris, Kaminsky and Simard,[114] who studied the absorption spectra of the leucocyanides and products of photolysis of malachite green, found the Lifschitz mechanism inadequate to account for the phenomenon of fading of the color. They found the addition of water to the alcoholic (95-per cent) solutions to increase the rate of fading, which could be similarly accelerated by potassium hydroxide or cyanide. No dark reaction could be observed if hydrochloric acid was added either before or after the photochemical production of the color. The addition of the acid to partly faded solutions restored the color completely, unless the water content of the solutions exceeded 20 per cent, in which case there was only a 95 to 97 per cent restoration of the color. No color appeared when hydrochloric acid was added to a non-irradiated leuco-cyanide solution. This indicated that the product of the dark reaction in 95-per cent alcohol is not the original leucocyanide. In their modified mechanism, importance was attached to hydrolysis of the photocompound. In the absence of hydrochloric acid, the final product of the dark reaction was assumed to be the colorless carbinol and not the original leucocyanide. Accordingly, they proposed the following scheme:

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[109] Gros, O., *Z. physik. Chem.*, 37, 157 (1901).

[110] König, E., *Z. Angew. Chem.*, 17, 1633 (1904).

[111] Eder, J. M., *Phot. Korr.*, 56, 140 (1919); *Chem. Zentr.*, 90, 396 (1919); *J. Soc. Chem. Ind.*, 38, 878 (1919).

[112] Carroll, B. H., *J. Phys. Chem.*, 30, 130 (1926).

[113] Lifschitz, I., *Ber.*, 52, 1919 (1919); 58B, 2434 (1925); Lifschitz, I., and Joffe, C., *Z. physik. Chem.*, 97, 426 (1921).

[114] Harris, L., Kaminsky, J., and Simard, R., *J. Am. Chem. Soc.*, 57, 1151 (1935).

$$\begin{array}{ccc}
[(CH_3)_2NC_6H_4]_2C_6H_5{\equiv}C{-}CN & \xrightarrow[\text{Ia}]{\text{Light}} & [(CH_3)_2NC_6H_4]_2C_6H_5 \equiv CCN \\
\text{Colorless, non-dissociated} & & \downarrow \\
\text{II} \downarrow & & \{[(CH_3)_2NC_6H_4]_2C_6H_5{\equiv}C\}^+CN^- \text{ Colored} \\
[(CH_3)_2NC_6H_4]_2C_6H_5{\equiv}COH & \xrightarrow[\text{IV}]{\text{HCl}} & \downarrow \\
\text{Colorless, non-dissociated} & & \{[(CH_3)_2NC_6H_4]_2C_6H_5{\equiv}C\}^+Cl^- \text{ Colored.}
\end{array}$$

The carbinol can undergo a photolysis to the colored compound, which accounts for the regeneration by light of the partly decolorized solution. It was assumed that reaction I is instantaneous, but that reaction III may be slow or moderate. Reaction IV was known to be comparatively slow from measurements made with the pure carbinol. Reactions II and IV were found to be fast if hydrochloric acid was used during the photolysis. No evidence could be found for the formation of an intermediate compound in Ia. The dark reaction had a positive temperature coefficient. Ariga [115] observed also that the colorless solution of malachite green produced by the action of alkali rather than cyanide (probably a colorless pseudo-ammonium base) regains its color when irradiated by a mercury arc or intense sunlight. The unimolecular rate constant was independent of the alkali concentration and temperature, but was proportional to the light intensity.

The Lifschitz reaction was made the basis of a useful actinometric solution by Weyde and Frankenburger,[116] who used a pure alcoholic solution of the leucocyanide of crystal violet. The quantum yield of the color formation is unity for the wave-lengths 2537 and 3130A. If enough cyanide was added to insure reversal in darkness, the solution was found to be suitable for use by physicians and meteorologists for measuring the erythema-producing rays of sunlight or artificial sources. In the case of this dye, the reverse dark reaction has a temperature coefficient of five. Its rate is proportional to the dye concentration and is greatly diminished by the presence of a little water.

For a precision actinometer, Harris and Kaminsky [117] found the malachite green leucocyanide to be superior, since it has thirty times the solubility of the crystal violet leucocyanide. It was especially suited for the region between 3340 and 2480A. With malachite green, a shorter cell-length may be used with certainty of 99.9-per cent absorption, the correction for inner-filter action by the photocompound is less, and colorimetric measurements can be made more accurately for the green dye. The quantum yield is unity.

Relatively little is known of the bleaching of the triphenylmethane dyes.

[115] Ariga, T., *Bull. Chem. Soc. Japan*, **2**, 65 (1927); *Chem. Abs.*, **21**, 2103 (1927).

[116] Weyde, E., and Frankenburger, W., *Trans. Faraday Soc.*, **27**, 561 (1931); Weyde, E., Frankenburger, W., and Zimmermann, W., *Z. physik. Chem.*, **17B**, 276 (1932).

[117] Harris, L., and Kaminsky, J., *J. Am. Chem. Soc.*, **57**, 1154 (1935).

Henriquez[118] believed that exposure of aqueous crystal violet solutions for several days converts it into a red dye, assumed to be fuchsine, by a replacement of the methyl groups by hydrogen. The presence of a free amino-group could be proved by diazotation and coupling reactions. Under similar conditions, malachite green was believed to be converted into Doebner's violet. With visible light, these color changes were more rapid than the bleaching of the dyes, but ultraviolet light destroys the colors, the more rapidly the more basic the solution. The oxidation of fuchsine by hydrogen peroxide is also brought about by ultraviolet light, the amino-groups being unaffected. Iwamoto[119] states that in the presence of air and light, malachite green oxalate and crystal violet oxalate are converted into *p*-dimethylaminoacetophenone and Michler's ketone, respectively. In a sealed tube, the crystal violet oxalate gives the leuco- compound. Weyde, Frankenburger and Zimmermann[120] found that on prolonged irradiation of alcoholic solution containing potassium cyanide, the leucocyanide is completely destroyed, probably by oxidation.

Phthalein Dyes. The radiation of an arc light has been said to increase the rapidity of the oxidation of phenolphthalin to phenolphthalein.[121]

Fluorescein in glycerol solution exhibits a blue rather than a green fluorescence when irradiated by ultraviolet light. This is gradually and permanently lost on prolonged irradiation by wave-lengths shorter than 2540A. Glycerol solutions of methylene violet, corallin, crocein, esculin, erythrosin, eosin and rhodamine similarly lose their fluorescent properties on exposure to ultraviolet light. Solutions of erythrosine, eosin and rhodamine in benzyl alcohol are much more sensitive to the action of light than are the glycerol solutions.[122]

It has been suggested[123] that the bleaching of fluorescein dyes by light is a process of oxidation by hydrogen peroxide probably formed from water and oxygen, this reaction requiring an activation of the dye molecule by light.

Reychler[124] found no iodine liberated in darkness from solutions containing 0 125 gm. potassium iodide, 0.5 gm. of potassium dichromate and 0.01 gm. of eosin per 100 cc. in three hours. In weak diffused light after forty minutes the iodine liberated was equivalent to 2 8 cc. of 1-per cent sodium thiosulfate solution. After two and ten minutes in sunlight, the amounts of thiosulfate used were 6.3 and 16.4 cc.

In the presence of reducing agents, eosin is not hydrogenated[125] in darkness, even in warming. In sunlight or the light of a quartz lamp, it is almost instantly hydrogenated. The color returns quickly in darkness unless the irradiation has been unnecessarily prolonged, in which case the eosin is irreversibly changed into a strongly fluorescing substance.

Methylene Blue. Nurnberger and Arnow[126] find that aqueous solutions of methylene blue have two regions of absorption with maxima at 2920 and 2460A. Irradiation of the solution with a mercury arc causes a decrease in the absorption in the visible and ultraviolet, the effect being greatest in the solutions of highest pH. The wave-lengths most active in decreasing the absorption are shorter than 2700A. For this reason, the change in absorption by aqueous solutions of methylene blue cannot be used as a measure of the light intensity in the physiologically active region between 2900 and 3100A.

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[118] Henriquez, P. C., *Rec. trav. chim.*, **52**, 991 (1933).

[119] Iwamoto, K., *Bull. Chem. Soc. Japan*, **10**, 420 (1935); *Brit. Chem. Abs.*, **B**, 1090 (1935).

[120] Weyde, E., Frankenburger, W., and Zimmermann, W., *Z. physik. Chem.*, **17B**, 276 (1932).

[121] Rossi, G., *Chem. Zentr.*, **82**, 1659 (1911); *Giorn. Farm. Chem.*, **60**, 433 (1911).

[122] Asterblum, M., *Bull. Intern. Acad. Polonaise*, **A7-8**, 297 (1924); *Chem. Abs.*, **20**, 1562 (1926).

[123] Blum, H. F., and Spealman, C. R., *J. Phys. Chem.*, **37**, 1123 (1933); see also Chakravarti, D. N., and Dhar, N. R., *Z. anorg. Chem.*, **142**, 299 (1925).

[124] Reychler, A., *Bull. soc. chim. Belg.*, **34**, 236 (1925); *Chem. Abs.*, **20**, 544 (1926).

[125] Kögel, G., and Steigmann, A., *Phot. Ind.*, 1169 (1925); *Chem. Abs.*, **20**, 1035 (1926).

[126] Nurnberger, C., and Arnow, L., *J. Phys. Chem.*, **38**, 71 (1934).

Most photochemical studies on this dye have been concerned with coupled or sensitized processes. Brandt[127] studied the iron-sensitized reduction in the presence of ethanol and a phosphate buffer at pH 8.6. A considerable dark reaction occurred only when both alcohol and ferrous ions were present, and it was in such solutions that the greatest photosensitization was observed. The reduced solutions were reoxidized in the dark, an equilibrium being established which is displaced toward the side of leuco-methylene blue.

In light, zinc oxide acts on aqueous solutions of organic dyes of widely different classes.[128] In pure, air-free aqueous solution, the dyes are both oxidized and reduced. In the presence of an anodic depolarizer, they are exclusively reduced. With vat dyes, photolysis still occurs even at the highest reduction potentials, 0.15 v. in the case of safranine. A considerable difference in potential between the anodic and cathodic processes can be overcome by light. With azo-dyes, the photolytic reduction is not reversible, the products not reforming dyes on exposure to the air. Under certain conditions, sensitizing dyes can act upon other dyes as does zinc oxide. The necessary condition is that the absorption region of the sensitizing dye must coincide with that of the acceptor on the short wave-length side.

In the presence of zinc oxide as photosensitizer, Arro[129] found no vat dye formed during the bleaching of methylene blue. But in the presence of an anodic depolarizer (dextrose), the velocity of fading is increased and some vat dye is formed. The sensitizing action of yellow mercuric oxide is greater, and that of cadmium oxide, yellow lead oxide and the uranyl ion, less than that of zinc oxide. The addition of manganese dioxide, uranium dioxide or cadmium oxide increases the action of zinc oxide. The bleaching is irreversible.

Pyruvic acid, "Kojic" acid, ethyl acetoacetate, phloroglucinol and resorcinol reduce the dye in the absence of oxygen when irradiated.[130]

The enzymatic reduction of the dye by *Bacterium pasteurianum* and by liver extracts is also speeded up by light. The dye molecule and not the hydrogen donor or the dehydrase is activated in the photochemical reaction.

The equilibrium potential of the methylene blue and phenylhydrazine sulfonate reaction is light-sensitive,[131] the direction of the displacement of the equilibrium being opposite in light from the two ends of the visible spectrum. Hellström[132] has observed that the redox potential of the methylene blue-ferrous ion system decreases reversibly in light, the potential change being dependent on the pH. However, the potential of the iron-free 50-per cent reduced dye is not affected by light, and the addition of ferrocyanide does not make it photosensitive. Light activation of the dye may cause the formation of a methylene blue-iron complex.

A procedure advocated by Marie and Raleigh[133] for the treatment of methylene blue for use in biological stains consists in dissolving one gram in 100 cc. of aqueous 0.5-per ent sodium bicarbonate solution and exposing in an open shallow dish to an arc lamp or ten to thirty minutes. When cool, there is slowly added 500 cc. of 0.1-per cent ellowish eosin solution until the surface becomes purplish with a metallic luster and a ine black powder is formed on the surface. After filtering and air-drying 0.1 gram is lissolved in 60 cc. of acetone free from methanol.

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[127] Brandt, K. M., *Arkiv Kemi, Mineral Geol.*, **12B**, No. 7 (1935); *Chem. Abs.*, **30**, 386 (1936); see also Weiss, J., *Trans. Faraday Soc.*, **32**, 1331 (1936).

[128] Neuweiler, C., *Z. wiss. Phot.*, **25**, 187 (1928); *Brit. Chem. Abs.*, **1928A**, 457.

[129] Arro, H., *Commentationes Univ. Tartu* **A18**, (5) 3 (1930); *Chem. Abs.*, **26**, 4255 (1932).

[130] Tamiya, H., Hida, T., and Tanaka, K., *Acta Phytochim.*, **5**, 119 (1930); *Chem. Abs.*, **25**, 1531 (1931).

[131] Holst, G., *Z. physik. Chem.*, **A175**, 99 (1935); **179A**, 172 (1937); *Nature*, **139**, 285 (1937).

[132] Hellström, H., *Naturwiss.*, **24**, 76, 217 (1936).

[133] Marie, S. V., and Raleigh, J. T., *J. Lab. Clin. Med.*, **10**, 250 (1924).

Irradiation of methylene blue, thionine, or brilliant cresyl blue in acid ferrous ulfate with the visible light of a strong carbon arc produces bleaching or a change n color, due to the formation of leuco- dyes, which is irreversible if the ferric ion ormed is precipitated by hydrolysis. In darkness, the process is completely reversible, the ferric ion being reduced by the leuco- dye.[134] In the absence of the dye he irradiation of a 0.5 molar solution of ferrous sulfate in sulfuric acid by a trong mercury arc produces hydrogen when oxygen is excluded.

The rate at which Lauth's violet is bleached in aqueous methanol solution in he presence of diethyl-β-allylthiocarbamide as acceptor rises rapidly toward a imiting value as the concentration of the latter is increased, and at the same time he temperature coefficient falls. Hydroquinone, pyrogallol, and phenol retard the bleaching and also reduce the fluorescence of sodium naphthionate, the relative efficiencies being similar in each case. The part played by these substances in both processes depends on the deactivation of activated molecules by collisions. At high concentrations, electrolytes either accelerate the bleaching somewhat or retard it but slightly, although with small concentrations of some salts, there is a pronounced retardation.[135]

If a 0.001-per cent aqueous solution of Lauth's violet (thionine) containing a small amount of ferrous sulfate (0.0075 mole per liter) and 0.01 molar sulfuric acid is cooled to −10°C. and exposed to the light of a powerful arc light, the dye is bleached in one or two seconds by a reversible process. The higher the temperature and the weaker the light, the slower the reduction. Lauth's violet has a positive reduction potential, 0.045 v. Methylene blue, Nile blue, phenosafranine and neutral red, all of which have negative normal reduction potentials, do not behave in a similar manner. In the case of methylene blue, photoreduction occurs if the ferrous sulfate is replaced by potassium ferrocyanide, which has a more negative reduction potential. The phenomenon can be explained by supposing that the photoexcited molecule (Lauth's violet) has a more positive reduction potential than the unexcited molecule, and even more positive than that of the ferric-ferrous ion system. Therefore, a reaction can occur with the formation of leuco- base and ferric ion. The maximum of the absorption band of Lauth's violet at 6000A corresponds to an energy (47,370 cals. per mole) more than sufficient for the above change. Methylene blue has a more negative reduction potential than Lauth's violet and its absorption maximum lies at longer wave-lengths (6700A) so that the energy absorbed is insufficient for the reaction to occur.

Bleaching of Dyes. The rate of loss of color of indigocarmine in ammonium oxalate solution by atmospheric oxidation under the influence of violet light obeys the law of mass action for concentrations ranging between 1 per cent and one to twenty thousand.[136] Similarly, the oxidation of helianthine follows the law, even in the range of concentrations in which solutions exhibiting an appreciable fluorescence do not follow it.

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[134] Weiss, J., *Nature*, **136**, 794 (1935). See, however, Weber,[137] Leuco methylene blue turns blue in the light and is decolorized by standing in the dark, according to Matiu, A. I., and Popescu, C., *Bull. soc. chim.*, **4**, 1230 (1937). This had been previously observed by W. M. Clark, *U. S. Public Health Reports*, **40**, No. 23, 1131-1201 (1925).

[135] Weber, K., *Z. physik. Chem.*, **15B**, 18 (1931); *Naturwiss.*, **23**, 849 (1935).

[136] Perrin, J., and Choucroun, N., *Compt. rend.*, **187**, 697 (1928).

An increase of temperature between 15 and 45°C. retards the photochemical decolorization of benzene solutions of cyanine and gallocyanine.[137]

Aside from the detailed studies which have been made on the photochemistry of individual dyestuffs, there have been many observations of the bleaching of dyestuffs in general. Some have contributed essential data on the relative light-fastness of different classes of dyestuffs. Others have been more or less speculative but have in some instances at least brought forward stimulating suggestions as to the mechanisms concerned.[138]

Steigmann[139] raises the question as to why certain dyes are light-fast despite the absorption of energy by their chromophores. He suggests that in certain cases there may be a preferential action on other light-sensitive groups present in the molecule which cause an "intra-molecular desensitization." For this he considers alizarin an example. In other dyes, certain other groups, or configurations may exert an inhibitory action, but in this case the nature of the transformations of the absorbed energy is obscure.

Although some workers have found light to convert certain dyes, particularly of the triphenylmethane series, into other dyes, Barat and Dutt[140] find that, in general, sunlight decomposes dyestuffs directly into colorless products In other words, the net effect is practically the same as that of a gradual dilution of the dye solution until its color becomes invisible. Spectrophotometric studies of the bleaching of a number of dyes have been published by Alberts.[141]

Leiber[142] studied the effect of daylight in altering the absorption spectra of films of dyed gelatin made by pouring 10 cc. of an 8-per cent solution of the dye over a 100 sq. cm. glass mold. The dyes fell into three classes: (1) Bleaching makes the dye density gradually decrease. (2) A region of strong absorption was decreased and a field of weak absorption was strengthened. (3) The absorption maximum was displaced to other wave-lengths. The latter two classes were not entirely distinct. The following dyes were not affected by exposure to sunlight for 28 days and are suitable for the preparation of photographic filters: Crystal Ponceau 6R, Orange II, Pyrazole Yellow, Rapid Filter Yellow, Naphthol Green, Toluidine Green and Toluidine Blue.

The change of conductance of collodion films colored by cyanine, pinaverdol and pinachrome was observed by an electrometric method by Zchodro[143] during illumination. The collodion itself is unaffected by white light. The conductivity of the film increases with the time of illumination and at first is proportional to the time, but on longer exposures, the increase becomes less rapid and the conductivity gradually reaches a constant value. After the illumination ceases, the conductivity gradually diminishes. Cyanine showed a maximum conductivity at around 6000A, pinaverdol at about 5700A and pinachrome a sharp maximum at about 5800A. Irradiation of a solution of cyanine in benzene produced a decrease in its electrical resistance, which rose again when the illumination ceased. Illumination with monochromatic light had this effect only when its wave-length was in the absorption band of the solution. Kosche[144] finds Indigosol IBL darkens in light, probably because of oxidation. Not all indigosol dyes are light-sensitive.

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[137] Zchodro, N., *J. chim phys.*, **26**, 178 (1929); *Chem Abs.*, **23**, 3166 (1929).

[138] Kögel, G., *Phot. Korr*, **68**, 83 (1932); *Chem. Abs*, **26**, 5507 (1932).

[139] Steigmann, A., *Z. wiss Phot.*, **27**, 268 (1929); *Brit. Chem. Abs.*, **A**, 174 (1930).

[140] Barat, K., and Dutt, S., *Quart. J. Indian Chem. Soc.*, **4**, 265 (1927); *Chem. Abs.*, **21**, 3194 (1927).

[141] Alberts, H., *Z. wiss. Phot.*, **33**, 234, 249 (1935).

[142] Leiber, F., *Kolloid-Z.*, **50**, 68, 117 (1930).

[143] Zchodro, N., *J. chim. phys.*, **26**, 59, 117 (1929); *Chem. Abs.*, **24**, 1578 (1930).

[144] Kosche, S., *Klepzig's Textil-Z.*, **40**, 584 (1937); *Chem. Abs.*, **32**, 6465 (1938).

Crespi[145] found no parallelism between the action of solar and ultraviolet radiation in their effects on cotton dyes. Ozone formation played no part in the action of the latter radiation. Evidence in support of an oxidation mechanism has been advanced by several workers. Scharwin and Pakschwer[146] exposed methylene blue, crystal violet, Congo red and eosin on cotton or paper in glass tubes in which were sealed various gases, to the action of sunlight or the light of a mercury arc. The speed of bleaching decreased in various gases in the following order: oxygen, nitric oxide, nitrous oxide, carbon monoxide, carbon dioxide, hydrogen, nitrogen. No bleaching was observed under nitrogen and generally none with hydrogen, although in the latter case, decided changes due to reduction sometimes occurred. In oxygen, nitric oxide and nitrous oxide, carbon dioxide could always be detected after the exposure to sunlight. The changes due to oxidation were irreversible. When the dye was absorbed in porous clay, the amount of carbon dioxide produced after four months in sunlight was much less than in cases in which cotton was the substrate.

It has recently been pointed out that in practice consideration must be given not so much to the effect of light on a dye as to its effect on the entire fiber-dye system. A single dye may also fade, but may be permanent when present in admixture with a more resistant dye.

An early theory of the bleaching mechanism due to Gebhardt[147] assumed the intermediate formation of an organic peroxide of the dye, but not of hydrogen peroxide. The earlier literature of the fading of dyes on cotton fabrics was reviewed by Cunliffe.[148]

Plain calico and similar fabrics dyed with Brilliant Copper Blue, Chlorazol Sky Blue and Benzopurpurin 4B were found by Miss Hibbert[149] to have almost unchanged copper numbers after exposure to 669 hours of bright sunshine. Since complete destruction of the dyes occurred long before the copper number of the fabric reached 3.6, it was concluded that the fading of dyed cotton is not due to a reducing action of the cellulose under the influence of light, as had been previously assumed.[150] Certain dyes retard or accelerate the tendering of cotton. Cotton fabrics dyed with Duranthrene Yellow, Cibanone Yellow and Indigo, which had an original tensile strength of 48 lbs. had tensile strengths of 27, 16 and 22 lbs., respectively, after exposure for 120 hours in a Fade-Ometer Isatin could be obtained in a pure state by extraction from calico which had been dyed with indigo and exposed to light.[151] In cotton materials dyed with chrome green, chromium hydroxide had a marked protective effect against sunlight.

According to Seyewetz and Mounier,[152] nitrated coloring matters turn brown under the action of light, which probably has a reducing action. The brown substance is insoluble in water and slightly soluble in alcohol, but too little could be isolated for its composition to be determined.

Cotton fabrics dyed with *o*-tolueneazo-β-naphthol became covered with bright lustrous crystals after exposure for three minutes to the light from a Fade-

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[145] Crespi, F., *Atti congresso naz. chim. pura applicata,* **2,** 833 (1926), *Chem Abs.,* **22,** 3532 (1928).

[146] Scharwin, W., and Pakschwer, A., *Z. angew* Chem, **40,** 1008 (1927).

[147] Gebhardt, K., *Z angew. Chem.,* **22,** 2484 (1910); **23,** 820 (1910); *J. Chem. Soc.,* **98,** 405 (1910).

[148] Cunliffe, P. W., *J. Textile Inst.,* **15,** 173; see also Ellis, G. H., *Chem. Age.,* **13,** 470 (1925); Barker, S., and Hirst, H., *J. Textile Inst.,* **17,** 483T (1926).

[149] Hibbert, E., *J. Soc Dyers Colourists.* **43,** 292 (1927); *Chem Abs.,* **43,** 292 (1927); *Brit. Chem. Abs.,* **B,** 840 (1927).

[150] See Harrison, W., *Ber*, **47,** 689 (1914).

[151] See also Haller, R., Hackl, J., and Frankfurt, M., *Textilber.,* **9,** 415 (1928); *Brit. Chem. Abs.,* **B,** 479 (1928). In contrast to Indanthrene Yellow, the fading of indigo is a process of oxidation.

[152] Seyewetz, A., and Mounier, D., *Compt. rend.,* **185,** 1279 (1927); *Bull. soc. chim*, **43,** 648 (1928); *Chem. Abs.,* **22,** 916 (1928).

Ometer.[153] The crystals were shown capable of sublimation and when recrystallized from chloroform were obtained as crystals of a different character but the same melting point as that of *o*-tolueneazo-β-naphthol. A thin layer of the powdered compound sublimed to only a very small degree at 45°C., the temperature reached in the irradiation, and it was not possible to obtain crystals as in the case of the dyed fabric. The cotton fabric suffered a loss of color due to this sublimation in the Fade-Ometer, but it did not change in color or become dull as it does when exposed in sunlight. Sublimation effects were observed also with cotton dyed with *o*-tolueneazo-α-naphthol and with combinations of Naphthol AS-BO and AS-RL with Fast Orange G base, but no crystals were formed on the surface.

Curtis[154] states that solutions of aniline green and magenta are not bleached when exposed to a quartz mercury arc. Neither are they bleached by the addition of 3-per cent hydrogen peroxide until the mixture is rayed. It was possible to exclude ozone as a cause of the bleaching. Holmes[155] reports that solutions of magenta, malachite green, methyl violet and crystal violet which had been decolorized by sulfur dioxide develop their original colors when exposed to ultraviolet rays of wave-lengths shorter than 3300A.

The photo-oxidation of many dyes by potassium dichromate was studied by Plotnikov.[156] Aqueous solutions of the following dyes were not affected: trypan blue, induline, dahlia, aniline green, malachite green, naphthol green, iodine green, nigrosin, trypan red, erythrosine, indigocarmine blue, gentian violet, Guinea green B and G, Brilliant Safranine, Aurantia, safranine, lithion carmine, carmine II, rose Bengal, Rhodamine B, Hofmann violet, methyl violet, crystal violet, cresyl fast violet. On the other hand, ethyl green, cyanin and naphthalene blue change very rapidly, both in light and darkness. Nile blue and cresyl blue 2BS are stable in darkness even on boiling, but in light change fairly quickly to bright red, fluorescent substances.

TESTS FOR THE LIGHT-FASTNESS OF DYES

The reproducible determination of the light-fastness of a dye or the relative light-fastnesses of a series of dyes requires the consideration of several factors. The distribution of the energy available at various wave-lengths in the light of the source employed for the test is of the utmost importance for the rapidity and reproducibility of the results. In some dyes, the absorption is predominantly in the visible; in others there are additional bands in the ultraviolet. Furthermore, the absorption spectrum and photochemical behavior of a dye in pure solution or in a collodion film may differ from that which it exhibits when applied to a fiber. In addition, the absorption of light by the fiber must be taken into account, since it may either lessen the amount of light available for the destruction of the dyestuff or it may cause photochemical changes in the fiber which result in the production of products which may hasten or retard the fading of the dye. The intensities of the radiations at various wave-lengths in sunlight vary extremely with the location at which the tests are conducted, with the time of year and with the amount of cloudiness, dust, smoke, etc. Variations in temperature, humidity, and the presence of acid fumes, also complicate the results of sunlight fading tests. As a result, it is difficult to secure reproducible results in successive tests at a given station, and far more so to make the results at one station compare with those obtained at another geographical location. For these reasons, exhaustive studies have been made by a Subcommittee on Light-fastness of the American Association of Textile Chemists and Colorists[157] to find a substitute for sunlight whose fading action will have speed, similarity to the action of the sun, and a capacity for exact reproduction at different times and places. Similar investigations have been undertaken in other countries.[158] Recent workers have tended to emphasize the unsuitability of most artificial sources for giving results directly comparable with those of actual sunlight fading, since the effects in the latter case are predominantly due to absorption of visible rays, whereas the artificial sources most frequently advocated usually produce either disproportionately large amounts of the longer ultraviolet radiations of sunlight or even radiations of wave-lengths shorter than those available in sunlight.[159] Accordingly much effort has recently been expended in improving the sunlight test. Hibbert[160] observed that certain colors dyed on cotton and Cellophane exhibited very different fading rates when exposed to sunlight or to ultraviolet rays. The larger the proportion of short ultraviolet rays in the source employed, the greater the attack on the cellulose. This produces reducing substances which may affect the dye. Harrison[161] observed that in vacuum under a mercury arc, cellulose reduced flavanthrene and many direct colors, the cellulose being itself oxidized. In sunlight, however, the cellulose is less rapidly attacked, and this explains why direct colors fade much more slowly in sunlight. The direct colors are said not to fade in the absence of the fiber, and wool is not as powerful a reducing agent for them as is irradiated cellulose. On the other hand, Harrison found basic colors to fade usually by oxidation processes, although fading by reduction may occur under certain conditions. Thus it is apparent that the nature of the substrate, as well as the spectral energy distribution, is involved in determining the results of fading tests.

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[153] Hibbert, E., *J. Soc. Dyers Colourists*, **44**, 300 (1928); *Brit. Chem. Abs.*, **B**, 854 (1928).

[154] Curtis, H. A., *J. Am. Chem. Soc.*, **42**, 720 (1920); *J. Chem. Soc.*, **118**, 342 (1920).

[155] Holmes, E. O., Jr., *J. Am. Chem. Soc.*, **44**, 1002 (1922).

[156] Plotnikow, J., *Z. Elektrochem.*, **32**, 13 (1926).

It has frequently been stated that deep shades are faster than pale shades. Barker, Hirst and Lambert[162] stated that measurements of the proportional losses of the predominant color in worsted fabrics dyed to different depths of shade with each of fifteen acid, mordant, and direct dyes, produced by sunlight and by light from a Fade-Ometer showed that the loss of color during fading was independent of the depth of the shade. Since the total color loss is the same for all shades, it is a much higher percentage of the total color in the pale than in the deep shades. Recently, however, attention has been called to the existence of a possibility that dyes exhibit a maximum sensitivity to light when present on the fibers at a certain concentration called the "mean critical tone." Pinte[163] believes that all comparative tests should be made at the previously determined "mean critical tone," since the fastness of a color improves the further it is from this value, whether toward zero, or 100. It is approximately 55 per cent for yellows, 45 per cent for oranges, 40 per cent for reds, and 35 per cent for violets, blues and greens.

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[157] Cady, W. H., *Proc. Am. Assoc. Textile Chem. Colorists*, 225, 1925; *Am. Dyestuff Rept.*, **14**, 58; *Chem. Abs.*, **18**, 906 (1924). For general discussion on light-fastness tests, see Jameson, C. W., *Am Dyestuff Rept.*, **21**, 306 (1932); Goodings, A. C., *Am Dyestuff Rept*, **24**, 663 (1935); Pestalozzi, S, *Zellstoff und Papier*, **17**, 53 (1937); *Chem. Abs.*, **31**, 3283 (1937); Déribéré, M., *Tiba*, **13**, 173, 175, 259, 329, 331, 415, 417, 481, 547, 549, 607, 687 (1935). Schupp, E., *Monatsh. Seide, Kunstseide*, **41**, 441, 488 (1936); Ris, H., *Klepzig's Textil-Z*, **39**, 731 (1936); Rein, H., *Ibid*, **39**, 732 (1936); Beil, A., *Angew. Chem.*, **49**, 905 (1936); Hirst, H. R., *J. Soc Dyers Colourists*, **41**, 347 (1925); Merck, O, *Farben Ztg*, **34**, 1117 (1929).

[158] Lantz, L. A., and others, *Fastness Committee, Society of Dyers and Colourists*, 52 pp., 1934; *Chem. Abs.*, **28**, 7538 (1934).

[159] Rein, H., *Angew. Chem.*, **47**, 157 (1934).

[160] Hibbert, E., *J. Soc. Dyers Colourists*, **48**, 251 (1932), *Chem Abs.*, **27**, 192 (1933).

[161] Harrison, W., *J. Soc. Dyers Colourists*, **28**, 225 (1912).

[162] Barker, S. G, Hirst, H. R., and Lambert, P. N., *J. Soc. Dyers Colourists*, **43**, 264 (1927); *Chem Abs.*, **21**, 3746 (1927).

[163] Pinte, J., *Chambre Commerce Roubaix Lab. recherches ind.*, No. **25**, 10 (1935); *Chimie et industrie*, **34**, 923; *Chem. Abs.*, **30**, 1234 (1936).

Humidity is also an important factor. Hedges [164] observed that the fading by a Hanovia mercury arc of wool patterns dyed with Ponceau RG, Acid Green G and Cyanin B under various conditions of humidity indicated an increased fading with increased humidity of the atmosphere surrounding the dyed patterns. The losses for these three dyes were for Ponceau RG at 52 and 100 per cent relative humidities, 1.5 and 4.9 per cent, for Acid Green G at 33 and 100 per cent, 11.2 and 21.7 per cent, and for Cyanin B, at 24 and 100 per cent, 23.8 and 41.0 per cent.

It is also important to agree upon the use of a definite method for determining the extent to which fading has occurred in a test. Many methods have been suggested. Gebhard [165] recorded the change of color, whether fading or change to another tint, by orthochromatic photography, using a light filter of the same color as the original dyeing. Appel and Smith [166] recorded the fading in the form of quantitative reflection measurements. Bravo [167] used a Pulfrich step photometer with that one of three spectral filters which most nearly coincided with the predominant color of the dye in making his observations. Mougeot [168] preferred a Toussaint photocolorimeter and believed "etalons" unsatisfactory. Niederhauser [169] recommended the use of a photocolorimeter and, in the exposure the Toussaint and Pinte "insolameter," which excludes dispersed daylight and measures the amount of light received by the illuminated materials. Probably the greater number of observers rely upon a simple visual comparison of the faded material with dyed patterns retained in darkness as standards. Hirst, in an earlier period,[170] indeed, considered such results as of more value than those obtained with the instruments then available.

Sunlight Tests. Much evidence has been accumulated as to the effects of variations of weather conditions on these tests; the data is so extensive that the original papers must be consulted. Barker and Hirst [171] investigated the effects on patterns on worsteds dyed with Victoria Blue and 85 other dyes, of sunlight during the months January to June in Leeds and in the country nearby, and also under five different cloud conditions. Full sunlight caused a fairly constant relative fading of Victoria Blue. Dull light had about one-tenth the effect of full sunlight. With Wardle, they charted the comparative sunlight values for different hours of the day for the six months included.[172] The value of the light for the total period of exposure could be expressed, by the aid of their graphs, in terms of what they considered a definite unit, one hour of June midday sun. For the variations of sunlight in the United States, and the differences between sunlight and the light of various artificial sources, see Anderson.[173]

Cady [174] found the angle of exposure to be important, the fading being greatest with horizontal exposures and less in order with 45° and with vertical ones. The angle of exposure is important only when total fading is considered; it has little effect on relative fading. Covering the samples with glass has effects which differ with different dyes. The effect of free circulation of air or the lack of it cannot be ignored. Continuous exposure produces different fading from that due to exposure only to the high cloudless sun. Direct sunlight has a different effect from skylight without sun. Exposures made in different localities show little variation in relative fading.

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[164] Hedges, J. J., *J. Soc. Dyers Colourists*, **43,** 261 (1927); Hill, L., *Ibid.*, 296, Cunliffe, P W., *Ibid.*, **45,** 215 (1929); *Chem. Abs.*, **21,** 3746 (1927); **23,** 4824 (1929).

[165] Gebhard, K., *Farben. Ztg.*, **22,** 6 (1911), various methods have been discussed by Cunliffe, P. W., *J. Soc. Dyers Colourists*, **45,** 215 (1929).

[166] Appel, W. D., and Smith, W. C., *Proc Am. Assoc. Textile Chem. Colorists*, 180 (1928), *Chem Abs*, **22,** 3048 (1928).

[167] Bravo, G. A., *Boll ufficiale staz. sper. ind. pelli mat. concianti*, **8,** 50 (1930); *Chem. Abs.*, **24,** 2888 (1930); *Boll. ufficiale staz. sper. ind pelli mat. concianti*, **9,** 210 (1931); *Chem. Abs.*, **26,** 2321 (1932).

[168] Mougeot, P., *Bull. soc. franç. elec.*, **5,** 965 (1935); *Chem. Abs.*, **30,** 4676 (1936).

[169] Niederhauser, *Klepsig's Textil. Z.*, **39,** 739 (1936); *Chem. Abs.*, **31,** 1623 (1937).

[170] Hirst, H. R., *J. Soc. Dyers and Colourists*, **41,** 347 (1925); *Brit. Chem Abs.*, **1926B,** 43.

[171] Barker, S. G., and Hirst, H. R., *J. Textile Inst.*, **17,** 483T (1926); *J. Soc Chem. Ind. Suppl* 976 (1926).

[172] Barker, S. G., Hirst, H. R, and Wardle, G. C, *J. Soc. Dyers Colourists*, **43,** 324 (1927).

[173] Anderson, W. T., Jr., *Proc. Am. Assoc. Textile Chem. Colorists*, 273 (1928). Note also Appel, W. D., *Ibid.*, 275, and Cady, W. H., and Appel, W. D., *Ibid.*, 179 (1927).

[174] Cady, W. H., *Proc. Am. Assoc. Textile Chem. Colorists*, 225 (1925); *Chem. Abs.*, **20,** 668 (1926).

Barker and Hirst[175] described an exposure cabinet for protecting the patterns from dirt, soot and rain. As a transparent, protective screen they employed Vita glass (see Chapter 10). Cady and Appel[176] recorded the energy received by some of the samples with the aid of a barium photoelectric cell and automatic recorder. They found that approximately reproducible relative fadings could be obtained in a series of dyeings exposed in widely separated stations in the United States at different times in the year at an angle of 45° from the horizontal, facing south, between 9 A.M. and 3 P.M. on sunny days only, in a cabinet covered with a good grade of window glass approximately one-eighth inch thick. The cabinet was open at the sides and the distance between the glass and the samples not less than one-half rich. They felt that no artificial light source could be recommended. The quantity of radiant energy as recorded in some of the exposures did not correspond to the amount of fading produced. In later work embracing 1252 dyeings on cotton, wool, silk and weighted silk of 381 different coloring matters[177] they found the presence or absence of a glass cover to have a marked effect on the fading in only 4 per cent of the samples. Earlier observations by Pierce[178] had indicated that glass keeps out most of the active rays. Hirst[179] had suggested that dyes intended for outside purposes should be directly exposed to sun and weather and that those intended for inside indoor use should be exposed under glass. It would seem that the use of Vita glass would permit the fading of the small group of dyes not susceptible to the wave-lengths transmitted by glass without complicating the results in the case of other dyes by the use of radiations not present in the solar spectrum.[180] Appel and Smith[181] tested Corex, Vita and six other glasses on twenty samples determining the extent to which the fading was affected by the manner in which they change the distribution of the intensities at various wave-lengths. It was found that the visible and long-wave ultraviolet of sunlight were relatively more important in comparison with the shorter wave-lengths of sunlight than had been commonly supposed. As a result they considered window glass satisfactory for the standard sunlight test.

Hirst,[182] who favored the use of the usual five degrees of fastness selected as standards the following dyes, given in increasing order of fastness: 0.4 per cent Indigocarmine X (BDC). I. 1.5 per cent Ponceau RG (BDC). II. 2.75

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[175] Barker, S. G., and Hirst, H R., *J Soc Dyers Colourists*, **43,** 300 (1927), *Chem. Abs.*, **21,** 3747 (1927).

[176] Cady, W. H., and Appel, W. D., *Proc. Am. Assoc. Textile Chem. Colorists*, 179, 1927; *Chem. Abs.*, **22,** 319 (1928).

[177] Cady, W. H., and Appel, W. D., *Proc. Am. Assoc Textile Chem. Colorists*, 217 (1929); *Am. Dyestuff Rept.*, **18,** 407; *Chem. Abs*, **23,** 4824 (1929).

[178] Pierce, E. W., *Chem. Eng.*, 97 (1918); *Textile World J.*, Jan 12, 1918.

[179] Hirst, H. R., *J. Soc Dyers and Colourists*, **41,** 347 (1925); *Brit Chem. Abs*, **B,** 43 (1926).

[180] Griffith, I. O., and Jenkins, R. G., *J. Soc. Dyers Colourists*, **43,** 297 (1927) find plate glass as used in shop windows to transmit 90 to 95 per cent of the visible spectrum and a small proportion of the ultraviolet from 3500 to 3000A but scarcely any of that between 3000 and 2900A.

[181] Appel, W. D., and Smith, W. C., *Proc. Am. Assoc. Textile Chem. Colaurists*, 180 (1928); *Chem. Abs.*, **22,** 3048 (1928).

[182] Hirst, H. R., *J. Soc. Dyers and Colourists*, **41,** 347 (1925); *Brit. Chem. Abs.*, **B,** 43 (1926).

per cent Azorubine (Sand.). III. 4.5 per cent Kiton Red S (CAC). IV. 2.5 per cent Chlorazol Fast Red FG (BDC). V. Indigo Full Shade or Natural Green B (C).[183] Tables of the German, English and American standards of dyes for light stability have recently been given by Wahl.[184] The standard wool dyes were tested at stations all over the world and were found to be of value in comparing the light effects available at various localities for testing other dyes simultaneously.

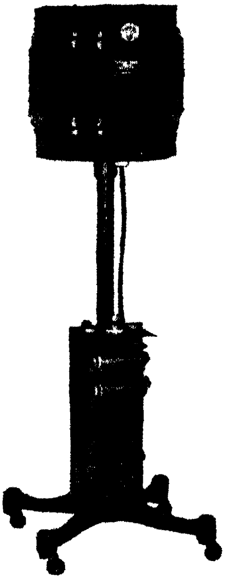

FIGURE 128.

Apparatus for Dye or Paint Testing.

Courtesy Cooper-Hewitt Electric Co.

Use of Artificial Sources. A number of early observers felt that the saving in time by and, they believed, greater reproducibility of the mercury arc as a source would more than compensate for any differences in fading which some dyes might exhibit under it.[185] Pierce believed that one hour under the mercury arc roughly paralleled an average day of exposure to sunlight. Apparatus of this type is commercially available (see Fig. 128) for both dye and paint testing. It consists merely of a circular cabinet about a vertical quartz mercury arc. The walls support removable panels to which the samples are attached. In comparing the action of the mercury arc with that of the sun, Scheurer,[186] who attempted to protect the dyes from any ozone formed, found that indigo resisted the mercury arc better than it did sunlight, although Benzo colors which were hardly faded by sunlight were materially changed by the mercury arc in 24 hours. After an extended study, Harrison[187] agreed not only that there are differences between the sun and the mercury arc effects but also that the effects are different with mercury arcs of high and of low intensity. Flynn[188] extended these results and also used a filter of 1.25 mm. of crown glass with the mercury arc. Fig. 129 illustrates the relative fading of dyes on cotton when exposed to sunlight, the direct and the filtered mercury arc. The dyes are represented as rectangular strips, the degree of fading being represented by the part of the strip cut out. The sunlight fading is at one end and the filtered mercury arc fading at the other. The intervening fadings represent the effect of one-half hour and one hour exposure by the direct mercury arc and show the reversal of the relative fastness between the direct and basic dyes when exposed to the unfiltered mercury arc. Under this source silk and wool appear to have less reducing action on dyes than has cotton.

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[183] Note also Deady, W. F., *Proc. Am. Assoc. Textile Chem. Colorists*, 242 (1925); Appel, W. D., *Am. Dyestuff Rep.*, **27**, *Proc. Am. Assoc. Textile Chem. Colorists* P 15 (1938).

[184] Wahl, A., *Rev. gén. mat. color*, **40**, 140 (1936); **41**, 460 (1937). See also Cunliffe, P. W., *J. Textile Inst.*, **28**, 203 (1937). For a new blue fastness scale. see Müller, E., *Klepzig's Textil Z.*, **39**, 732 (1936); Rein, H., *Angew Chem.*, **47**, 157 (1934). A standard should be adopted for interrelating fastness to light and to weather, according to Vendor, A., *Monatschr. Textil-Ind.*, **52**, 262 (1937); *Chem. Abs.*, **32**, 1458 (1938).

[185] Pierce, E. W., *Chem. Eng.*, 97, 1918; *Textile World J.*, Jan. 12, 1918; Flynn, O. R., *Am. Dyestuff Reptr.*, **12**, 837 (1923); Gebhard, K., *Farben Ztg*, **22**, 6 (1911).

[186] Scheurer, A., *Bull. soc. ind. Mulhouse*, **80**, 324 (1911).

[187] Harrison, W., *J. Soc. Dyers and Colourists*, **28**, 225 (1912).

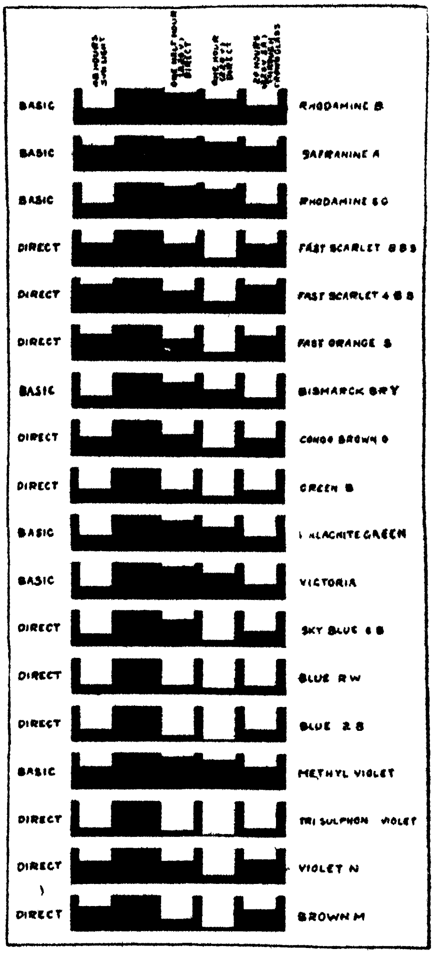

FIGURE 129.

Relative Fading of Dyes on Cotton.

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[188] Flynn, O. R., *Textile World*, 53, 25 (1923).

Iimori and Kitaoka[189] investigated the velocity of the bleaching of various dyes on cellulose acetate films before the mercury arc, but found it difficult to find one empirical equation which would express the behavior of every dye tested. Benzoic acid increased the rate of fading of methylene blue and disodium phosphate and calcium sulfate decreased it a little. For methyl violet, disodium phosphate, borax and quinine sulfate increased the rate slightly and calcium sulfate decreased it a little. Bravo[190] exposed a series of dyes on strips of filter paper at 50 cm. from a 2000 c.p. mercury lamp operated without a nickel oxide screen. The samples were ventilated to eliminate the possible influence of heat and ozone. One hundred and one dyes of the nitroso-, nitro- and azo- type were classified into four groups according to their resistance to bleaching. The very resistant dyes of Group I showed no change or only very slight changes after three hours. The resistant or medium-resistant dyes of Group II showed definite changes after two to three hours. Those of slight resistance (Group III) were altered in one to two hours. The non-resistant dyes of Group IV suffered intense changes in color or profound discoloration after one hour or less. Dyes of the nitro-, nitroso-, azo-, stilbene, pyrazolone, diphenylmethane and triphenylmethane, xanthene, acridine, quinoline, azine, oxazine and thiazine series were subsequently included. Bravo compared the percentage reflection at each of several wave-lengths photometrically with the corresponding values for a barium sulfate surface. In this way it was possible to study quantitatively the color changes which occur during fading.

Hill[191] found the fading of worsteds dyed with Indigocarmine X, Ponceau RG and Neolan Green B to be chiefly dependent on the ultraviolet of shorter wavelengths emitted by the mercury arc. A tungsten arc lamp of the Osram Co. of Berlin was claimed by Hochheim and Knebel[192] to have a spectral distribution very similar to that of normal sunlight and therefore to be superior to the mercury arc.

It was early found by Gordon[193] that results with the violet carbon arc compare more closely to those of average sunlight than do those with the mercury arc. They agreed more closely with those of average sunlight than the results of Arizona and New Jersey sunlight agreed with each other. The white flame carbon arc gave rather better results in some cases but was only half as rapid as the violet arc. Mott and Bedford[194] stated that for equal line energy, the effect of the white flame arc on Solio paper was five to six times better than that of a 110-volt quartz mercury arc operating at four atmospheres at 60 arc volts.

Recently there has been great progress in the development of carbons which yield definite reproducible distributions of energy in various spectral regions; these have been discussed in Chapter 5. Various forms of apparatus employing the carbon arc have been put upon the market. In one form,[195] a number of "swatch boxes" in which samples of fabrics, paints, etc. may be exposed under definite conditions of humidity are arranged around a carbon arc. They are mounted on trunnions which are hollow and serve to supply conditioned air to all the boxes in series. When any swatch box is thrown down for inspection, the rotation of the trunnion causes the air stream to be by-passed around that box.[196]

[189] Iimori, S., and Kitaoka, K., *J. Chem. Soc. Japan*, **48**, 479 (1927); *Chem. Abs.*, **22**, 1855 (1928).

[190] Bravo, G., *Bol. ufficiale staz. sper. ind. pelli mat. concianti*, **8**, 50, 184, 2928 (1930); **9**, 210 (1931). *Industria Chimica*, **9**, 313, 461 (1934); *Brit. Chem. Abs.*, **B**, 711 (1934); *Chem. Abs.*, **25**, 2295, 3173 (1931); **28**, 4238, 6316 (1934).

[191] Hill, L., *J. Soc. Dyers Colourists*, **43**, 296 (1927); *Brit. Chem. Abs.*, **B**, 839 (1927). Gordon, H. B., *Textile Colorist*, **43**, 29 (1921).

[192] Hochheim, E., and Knebel, E., *Textilber.*, **6**, 912 (1925); *Brit. Chem. Abs.*, **B**, 437 (1926); *Chem. Abs.*, **20**, 669 (1926). See also Appel, W. D., *Proc. Am. Assoc. Textile Chem. Colorists*, 246 (1925); *Am. Dyestuff Rept.*, **14**, 882.

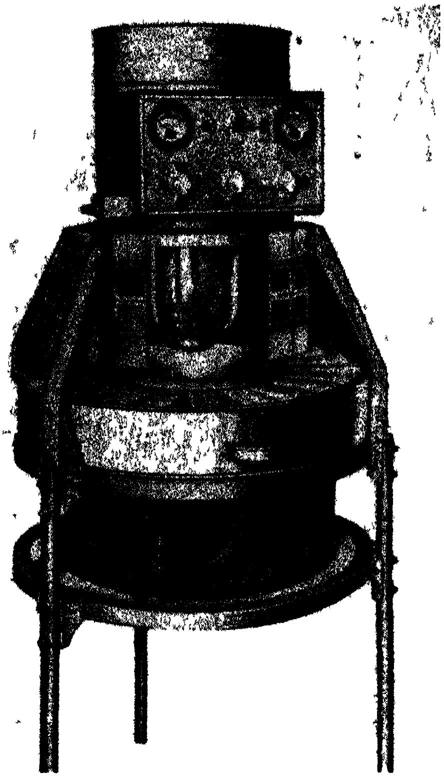
[193] Gordon, H. B., *Textile Colorist*, **43**, 29 (1921); *J. Soc. Chem. Ind.*, **40**, 149R (1921).

[194] Mott, W. R., and Bedford, C. W., *J. Ind. Eng. Chem.*, **8**, 1029 (1916). See also Cady, W. H., *Proc. Am. Assoc. Textile Chem. Colorists*, 42 (1925).

[195] King, F. A., British P. 309,726, April 2, 1928, to Kelvin, Bottomley and Baird Co.; *Brit. Chem. Abs.*, **B**, 461 (1929).

[196] For another form, see Hall, R. O., U. S. P. 1,969,606, to Ontario Research Foundation, and Bedford, E. F., *Silk J.*, **11**, No. 131, 38 (1935).

One of the most widely used types of commercial equipment is the Fade-Ometer (Fig. 130). In this, samples in metal specimen holders arranged in a circle are exposed to the light of a violet carbon arc enclosed in a 9200-PX glass globe. Ventilation is provided and the temperature is controlled by a thermostatically controlled blower. Textiles, papers and silks are generally tested between 98° and 104°F., but auto topping and similar materials are exposed at 140° to 150°F.



Courtesy Atlas Electric Devices Co

FIGURE 130.
Fade-Ometer, Type FDA.

A relative humidity of 42 to 60 per cent at the specimens is produced by wicks in a water reservoir placed below the specimen chamber. The air coming in contact with the specimens must filter through 1600 sq. in. of saturated wicking. The light from the source employed is so near that of sunlight that 95 per cent of a series of 40 dyes tested by it faded exactly as in sunlight or acceptably close to the sunlight fading. The light is somewhat more intense than sunlight so that for textiles one hour in the Fade-Ometer is equivalent to 1.3 hours of summer sunlight. For lithographic inks, 2.33 Fade-Ometer hours are approximately equivalent to six hours of sun exposure. In general for dyed textiles, 48 Fade-Ometer hours are equivalent to 10 days of summer or 180 days of winter sunlight. For printing inks, paper, etc., the 48 hour test is equivalent to 20 average days of summer or 360 days of winter sunlight.

Barker and Hirst[197] determined the fading of woolen and worsted patterns dyed with about 60 acid, direct, vat and mordant dyes in Indian, Ceylon and English sunlight and in the light of a Fade-Ometer. They used a Lovibond tintometer for direct visual comparisons and for measurements of the fluorescence in filtered ultraviolet light. By comparison of the fluorescence patterns it was possible to tell which samples had been faded in England, which in the tropics and which by the Fade-Ometer. The results in the latter case did not agree with those of exposure of the patterns to direct sunlight. Also less fading occurred in the tropics than in England. The discrepancies were attributed to the differences in the humidity.

The progressive loss of the predominant color in worsteds dyed with Indigo-carmine X, Wool Green S, Neolan Green B, Acid Violet 6B, Magenta and Ponceau RG and Chlorazol Blue B in the Fade-Ometer are given by the expression $t=\alpha l^n$ in which t is the time of exposure in hours, l is the percentage loss of predominant color, α is a constant which depends on the dye and n is 1.9 or 2.0. The actual and calculated color losses differ slightly during the early stages of fading.

Appel[198] recently concluded that the change in reflectance of some dyeings on exposure to light is not proportional to the intensity of the incident radiation, since when the intensity of the Fade-Ometer light was cut to one-tenth, the time required to produce a definite fading in different dyes was anywhere from two to ten times that required at the original intensity. Similarly, lowering the relative humidity from 75 to 31 per cent retarded the rate of fading of some dyes by a factor of two, but failed to affect the rate of fading of others.

Kinsman[199] employs the carbon arc and believes an exposure of 64 hours to be roughly equivalent to one month of summer sunlight. From comparisons of the results produced by the Fade-Ometer and sunlight, Griffith, Brode and Robertson[200] conclude the former (Type LV) to be a satisfactory substitute for the latter. Peach, yellow and green pure dyed Tru-hu silk crêpe and yellow, blue and rose Peter Pan gingham were used in their tests. The blue gingham did not fade in either the sun or the Fade-Ometer; the rose gingham faded more in the sun, particularly in the blue-green portion of the spectrum. The yellow gingham faded only after exposure to 150 hours of sunlight or in the Fade-Ometer. The peach, yellow and green silk crêpes faded to the same extent with both sources.[201]

Luckiesh and Taylor[202] noted that 23 silk ribbons exposed to sunlight and skylight at 3900 foot-candles for 11 hours, or to skylight alone at 450 foot-candles for 40 hours, showed as much fading as those exposed to 500 foot-candles from tungsten lamps for 100 hours. Approximately equal degrees of fading will result from exposure to the tungsten-filament radiation for 100 foot-candle hours, skylight for 34, or sunlight and skylight combined for 74.[203]

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[197] Barker, S. G., and Hirst, H. R., *J. Soc. Dyers Colourists*, **43**, 254 (1927); Barker, S. G., Hirst, H. R., and Lambert, P. N., *Ibid*, 263, *Brit. Chem. Abs.*, **B**, 811 (1927), Barker, S. G., *J. Textile Inst.*, **18**, 313 (1927); *Chem. Abs.*, **22**, 2059 (1928).

[198] Appel, W. D., *Proc. Am. Assoc. Textile Chem. Colorists*, 194, 202, 1935; *Am. Dyestuff Rept.*, **24**, 306, 314 (1935); *Chem. Abs.*, **29**, 5276 (1935).

[199] Kinsman, S. T., *J. Oil and Colour Chem. Assoc.*, **12**, 274 (1929); *Brit. Chem. Abs.*, **1930B**, 51.

[200] Griffith, M. E., Brode, W. R., and Robertson, H., *Ohio Agr. Sta. Bimonthly Bull.*, **169**, 143 (1934); *Chem. Abs.*, **28**, 7021 (1934).

[201] For a summary of early work on the suitability of various sources, see Hadfield, I. H., *J. Textile Inst.*, **18**, 527T (1927)

[202] Luckiesh, M., and Taylor, A. H., *Am. Dyestuff Rept.*, **14**, 613, 636 (1925); *Chem. Abs.*, **19**, 3597 (1925).

[203] For observations on the effect of ultraviolet on certain dyes, see McEwen, J. L., *Am. Dyestuff Rept.*, **21**, 337 (1932).

Various Types of Dyestuffs. Heermann[204] proposed to classify dye and textile fiber systems into four groups according to their susceptibility to light of various wave-lengths. These classes, termed "micro," "macro," "homo" and "mesotropic," are, respectively, most susceptible to light of short wave-lengths, long wave-lengths, all wave-lengths and to the ultraviolet rays of sunlight. Auramine, which is notoriously not fast to sunlight, resists short ultraviolet rays rather well.

In azo dyes,[205] the naphtha dyes having a hydroxyl group in the 2-position are superior to those in which it is in the 1-position. The exceptions are 1-naphthol-4-sulfonic acid, which is comparatively fast, and 2-naphthol-3,6-disulfonic acid, which is fugitive. The presence of two sulfonic acid groups in the naphthol nucleus does not decrease the fastness of the dyestuff. *p*-Sulfanilic dyes are more affected than *o*-sulfanilic acid dyes but less than *m*-sulfanilic acid dyes. The degree of darkening is little influenced by the presence or position of the sulfonic acid group in the benzene nucleus, although there is slightly less darkening in the *o*- and *p*-sulfanilic acid dyes. The combined effect of fading and darkening, which gives the total effect of light on these dyes, indicates that the *o*-sulfanilic acid dyes are superior to those made from aniline and *p*- and *m*-sulfanilic acids.

Kinsman[206] classifies lakes into five arbitrary groups according to the effects of light upon them. Group I, no perceptible alteration after one month in summer sunshine; II, slight loss; III, distinct loss in depth or alteration of shade; IV, distinct loss or alteration after 14 days; V, practically complete bleaching after one week. In practice, however, an accelerated test with a carbon arc was employed. Lakes belonging in the respective classes were as follows: I, Alizarin-red, aluminum calcium phosphate lake; II, Permanent-red 4B, calcium salt; III, Lithol-red R, barium salt; IV, Eosin YS, lead salt, barium sulfate base; V, lakes of fastness less than that of eosin. The carbon arc readings of these types are; unbleached after 240 hours, practically unbleached after 120 hours, bleached after 60 hours, bleached after 34 hours, bleached in less than 34 hours.

Wool patterns heavily dyed with Naphthol Yellow S, after exposure to sunlight until extensive browning had occurred, responded to a color test for 2-nitro-4-amino-α-naphthol-7-sulfonic acid, indicating the browning to be the result of photoreduction.[207] The slow bleaching of annatto solutions by air is much more rapid in light.[208]

If dyed Celanese is treated with such organic bases as dimethylaniline or diethylaniline, which absorb wave-lengths shorter than about 3400A, the light fastness of certain colors is improved. Colors strong in nitro- groups however, seemed to be deteriorated by this treatment.[209] The best protection for airplane wings is to dye the dope with spirit black.[210]

Colored Papers. Very similar methods are employed in testing the fading of dyes applied to paper. Appel and Bentzen[211] recommend the Atlas Fade-

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[204] Heermann, P., *Chem. Ztg.*, **48**, 813, 834 (1924). For recent reviews see H. Niimiya, *Chem. Rev. (Japan)*, **3**, 401 (1937); Pierce, F. W., *Rayon Textile Monthly*, **19**, 249, 263 (1938), Volz, K., *Spinner u. Weber*, **56**, No. 34, 43, 53 (1938).

[205] Griffith, M. E., *Ohio Agr. Expt. Sta., Bull. No* **548**, 80 (1935); Griffith, M. E., and Brode, W. R., *Ibid., Bull.* **565**, 3 (1936); *Am. Dyestuff Rept.*, **26**, 90 (1937); *Chem. Abs.*, **30**, 1565 (1936); **31**, 1211 (1937).

[206] Kinsman, S. T., *J. Oil and Colour Chem. Assoc.*, **12**, 274 (1929); *Chem. Abs.*, **24**, 737 (1930).

[207] Hodgson, H. H., and Smith, E. W., *J. Soc. Chem. Ind.*, **56**, 108T (1937); *Chem. Abs.*, **31**, 4500 (1937).

[208] Barnicoat, C. R., *J. Dairy Research*, **8**, 61 (1937); *Chem. Abs.*, **31**, 3581 (1937).

[209] Ellis, G. H., *Chem Age*, **13**, 470 (1925); *J Soc. Chem. Ind.*, **44**, 1093 (1925).

[210] First Report Fabrics Coördinating Research Committee, Dept. Sci. Ind. Research, 10 (1925); *Chemical Age (London)*, **13**, 331, 397 (1925).

[211] Appel, W. D., and Bentzen, T., *Paper Trade J.*, **88**, No. 9, 42 (1929); *Chem. Abs.*, **23**, 3095 (1929); Dalen, G., and Wilke, P., used the mercury arc, *Papier-Fabr.*, **26**, 199; *Chem. Abs.*, **22**, 2272 (1928).

Ometer, particularly the type equipped with a fan to prevent excessive heating of the sample. Grundy,[212] who also approved the method, noted that the exposed dyeings should be allowed to cool a short time before comparing the colors, since a slight change in shade may be due to the heat of the arc, rather than to fading. It did not seem possible to make standard numerical specifications for the light-fastness of colors on all qualities of paper. No basic colors were found which had sufficient fastness to receive consideration for the production of fast-to-light shades. With the ordinary type of soluble synthetic dyestuffs generally applied on paper, it seemed impossible to obtain fast shades on furnishes containing even small quantities of brown wood. The most suitable furnishes for fast-to-light shades are bleached sulfite, bleached soda, esparto, bleached rag, and under certain conditions unbleached sulfite, either individually or in mixture.

Loading materials affect the light fastness of dyes in paper,[213] partly because of the alkalinity of the filler. The pH of filled or unfilled papers is generally reduced by exposure to sunlight. Papers of lower pH values are the more easily faded. Dyes which are fast to light are generally acid resistant.

Riesenfeld and Hamburger[214] employed the time of exposure to a standard ultraviolet source required to produce a definite change in fluorescence as a measure of the relative light fastness of dyed papers.

Harrison[215] did not approve the use of the Grant method of following the reduction of fluorescence on irradiation, but could find no suitable inexpensive daylight lamp for comparing the samples. He proposed the use of bleached sulfite pulp, colored with graduated amounts of fast dyes, including the Chlorantin colors, or using one amount with additions of hexadecylpyridinium bromide to decrease the fastness. The sheets were then exposed to direct sunlight for 6, 12, 24, 48 and 96 hours and compared with controls or with irradiated controls without the addition of the deteriorating agent. He measured the light intensity to which the sample was exposed by an actinometric paper and a wedge-shaped slide transmitting graded amounts of light. This, when laid over a standard colored sheet, simulates the effect of graded bleaching. With this method, the best results were obtained with a pure rag paper, sized with 2 per cent rosin and 4 per cent alum, and dyed with Acid Rhodamin 3R.

Inks. Proposals have been made to employ ultraviolet radiations for testing inks by measuring the color of streaks on paper after exposure for two weeks to sunlight or for a shorter period to ultraviolet light.[216] The Bureau of Standards[217] recommended an exposure of 48 hours to ultraviolet light. A comparison streak of a standard ink was simultaneously exposed Turner[218] classified about fifty pigments into four groups according to their light fastness in printing ink.

Tests by Mitchell[219] did not substantiate the claim that ultraviolet fluorescence tests can be used for the differentiation of different types of inks or for the determination of their ages.

[212] Grundy, J. G., *World's Paper Trade Rev*, **101**, 1240, 1242, 1280, 1399, 1442 (1934); *Paper Maker and British Paper Trade J.*, **88**, No. 1, 138 (1934), *Chem Abs*, **28**, 7010 (1934).

[213] Pestalozzi, S., *Zellstoff u. Papier*, **15**, 496 (1935), *Chem. Abs*, **30**, 1558 (1936).

[214] Riesenfeld, E. H, and Hamburger, T, *Papier-Fabr*, **29**, 164 (1931); *Brit. Chem Abs.*, **B**, 625 (1931).

[215] Harrison, H. A., *Papier-Fabr.*, **34**, *Tech. Teil*, 321, 329 (1936); *Chem. Abs.*, **31**, 856 (1937); *Paper-Maker, TS* 54 (1936); *Chem. Abs*, **31**, 2428 (1937); *Svensk Papperstidn*, **39**, 352 (1936).

[216] Rupert, F. F., *Ind. Eng. Chem.*, **15**, 489 (1923), *J. Soc. Chem. Ind*, **42**, 612A (1923).

[217] *Bureau of Standards Circular* **95** (1920).

[218] Turner, J. S., *Am. Ink Maker*, **14**, No 1, 19 (1936); *Chem. Abs.*, **30**, 5817 (1936); Deeney, J. J., *Am. Ink Maker*, **11**, No. 2, 9, 23; No. 3, 13 (1933) *Chem. Abs.*, **27**, 5557 (1933)

[219] Mitchell, C. A., *Analyst*, **55**, 746 (1930).

Ink on freshly printed sheets dries faster when exposed at a distance of six inches from a mercury arc than in diffused lights, especially at higher temperatures.[220]

In making hectograph copying pads, a gelatinous mass (gelatin, water and glycerol) is treated with a minute proportion of a light-sensitive tanning agent such as ammonium dichromate and subjected to the action of ultraviolet light to effect tanning.[221]

Fluorescence Tests of Dyes. Hirst and King[222] found that certain Indigosol dyeings on wool showed in ultraviolet light a strong violet fluorescence on the original dyeing, but not on portions which had been exposed to light for some weeks. They suggested that the fluorescence might indicate incomplete oxidation and incomplete development since its intensity varied when different oxidizers were used. The method also could be used for indicating the degree of exhaustion of the dye-bath and was thought of value in the control of this type of dyeing. Kummerer[223] tabulated the fluorescence colors in ultraviolet light of variously dyed fabrics. The determination of fibers by their fluorescence colors is, according to Sommer,[224] subject to distinct limitations. For example, the dye present may entirely obscure the fluorescence color of the fabric or even lead to false conclusions. No certain distinction could be made between dyed flax and hemp. Bleached linen and cotton could not be distinguished nor could mohair and wool. Egyptian cotton is readily determined, as is dyed wool intended as a substitute for camel hair. Oil spots on fabrics are especially distinct. Alkali or acid damage to wool is not determinable by this method. After sulfite cellulose pulp has been exposed to a bright light it cannot be distinguished in this manner from soda pulp. The method cannot be used to identify coloring matters, according to Radley.[225]

TEXTILE PRINTING[226]

Haendel[227] described a process in which woven and knitted or plaited fabrics, leather and other materials are dyed or figured by treating them with light-sensitive compounds and subsequently exposing them to the action of light. Substances may be used which form dyes when exposed to light, such as mixtures of a sulfonated diazo- compound, *e.g.*, sodium phenyldiazosulfonate and an azo- component such as aniline hydrochloride. Light-sensitive substances which lose their capacity to form dyes when exposed to light may be used.

Designs may be applied to yarns, bands or fabrics of non-animal origin in a continuous operation involving application of a metal compound convertible photochemically into a compound in which the valence of the metal is different, exposure to ultraviolet light passing through a pattern, washing, conversion of either the altered or unaltered portion of the metal compound into a substance which cannot be washed out, washing and drying.[228]

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[220] Brown, R. A., *Am Ink Maker*, **9**, No. 3, 21 (1931); *Chem Abs*, **25**, 3500 (1931). The carbon arc is used by Arend. A. G., *Process Engraver's Monthly*, **44**, 173 (1937).

[221] Whitmore, W. B., U. S. P. 2,024,408, Dec. 17, 1935, to Ditto, Inc ; *Chem. Abs.*, **30**, 1156 (1936).

[222] Hirst, H. R., and King, A. T., *J Soc Dyers Colourists*, **43**, 266 (1927); *Chem Abs.*, **22**, 2276 (1928); *J. Textile Inst., Special No*, **18**, 369T (1927); *Chem. Abs*, **22**, 2061 (1928).

[223] Kummerer, L., *Melliand Textilber.*, **9**, 415 (1928). Sisley, P, [*Chimie et industrie, Special number 508* (March 1932)] gives data on 1200 dyes

[224] Sommer, H., *Melliand Textilber.*, **9**, 753 (1928); *Chem. Abs.*, **22**, 4825 (1928); compare de Buda, G., *Cuir tech.*, **21**, 98 (1932); *Chem. Abs.*, **26**, 3115 (1932).

[225] Radley, J. A., *J. Soc. Dyers Colourists*, **53**, 376 (1937); *Chem. Abs.*, **32**, 364 (1938).

[226] In the decoration of fabrics by the reducing action of light on silver salts, Michels, M, [German P. 441,690, May 4, 1926; *Bull. soc. ind. Mulhouse*, **94**, 124, 135 (1928); *Chem. Abs.*, **22**, 2468 (1928)] uses as a mordant for all basic dyes, a material formed from complex copper compounds.

[227] Haendel, W., British P. 309,166, April 7, 1928; *Chem. Abs.*, **24**, 509 (1930).

In an example, linen is passed through potassium dichromate solution, then over a rotary stencil containing one or more carbon arc lamps or mercury discharge tubes. treated with sodium alizarine sulfonate solution after passing through water, washing and drying.[229]

Freytag[230] showed that ultraviolet irradiation of solutions containing aniline hydrochloride and suitable oxidizing agents and catalysts as used in aniline black dyeing markedly accelerates the formation of the aniline black pigment. Satisfactory reproduction of images may be obtained by impregnating paper or cotton fabric with a 1- to 25-per cent solution of aniline hydrochloride containing five drops of aqueous 4-per cent potassium ferricyanide and 18 to 24 drops of 10-per cent aqueous sodium chlorate per 30 cc., covering with a photographic negative and exposing for fifteen minutes to ultraviolet light, and washing out unchanged aniline with water.

Similarly, solutions of either of the phenylenediamines produce a yellow or brown color formed by oxidation of the base. The naphthylamines behave in an analogous manner.[231] The process is assisted by the presence of about 1 per cent of an alkaline nitrate in the naphthylamine bath. With β-naphthylamine, the process is very rapid and will take place even in sunlight.

Freytag and Müller[232] also employed 2-benzyl pyridine, which becomes deep brown on exposure to light. Radiation of 2000 to 4000A converts it into a green dye. The compound is applied in 96-per cent alcohol and the solvent evaporated before making the exposure to light through a negative. The excess of unaltered compound is removed with dilute hydrochloric acid. The fastness of the photopyridine colors can be improved by coupling with diazotized bases.[233] After exposure for thirty to forty-five minutes at 30 to 50 cm. from a quartz lamp, the sample is passed through a boiling acid bath containing two to three per cent of a primary aromatic amine. The color thus obtained lacks fastness, but this may be improved by treating it without washing with a solution of a diazonium salt of an aromatic base. There is considerable change in the color.

Benzidine and tolidine on irradiation in the presence of sodium nitrate are oxidized on the fiber to fast dyes.[234] The samples of cotton and artificial silk so treated are coffee-brown with benzidine and yellowish-brown with *o*-tolidine. A number of amino-naphtholsulfonic acids have also been used.[235] The most suitable substances are the pyridines and the aniline salts of 8-nitro-1-naphthalenesulfonic acid. The best results are obtained when the exposures are made in a damp atmosphere.

Stabilized isodiazotate solutions[236] of aniline, *p* brom- and *p*-iodo- aniline, etc.

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[228] British P. 380,208, April 23, 1931, to N. V. Phillips Gloeilampenfabrieken; French P. 768,261, Aug. 3, 1934; *Chem Abs*, **27**, 3087 (1933); **29**, 621 (1935).

[229] For a general discussion of printing by photochemical processes, see Weickart, F., *Monatsh Seide, Kunstseide*, **38**, 474 (1933).

[230] Freytag, H., *Melliand. Textilber.*, **13**, 144 (1932); *Chem. Abs.*, **27**, 1834 (1933).

[231] Freytag, H., *Phot Korr.*, **69**, 184 (1933), *Chem. Abs*. **28**, 7538 (1934).

[232] Freytag, H , and Muller, A., *Monatschr. Textilind.*, **48**, 239, 273 (1933); *Chem. Abs.*, **28**, 5245 (1934).

[233] Freytag, H., *Monatschr. Textilind.*, **48**, 107, 130 (1933); *Chimie et industrie*, **31**, 621; *Chem. Abs.*, **28**, 3590 (1934).

[234] Freytag, H., and Preiss, S., *Monatschr. Textilind.*, **49**, 209, 231 (1934); *Chem. Abs.*, **29**, 2362 (1935).

[235] *Monatschr. Textilind.*, **49**, 262 (1934); *Chem. Abs.*, **29**, 2362 (1935); *Phot. Korr.*, **71**, 52 (1935).

[236] Oddo, G , Indovina, R., Albanese, G., and Amatore, G., *Gazz. chim. ital.*, **65**, 939 (1935); *Chem. Abs.*, **30**, 3792 (1936).

again acquire the power of coupling after thirty minutes of exposure to sunlight, ultraviolet light or an ordinary incandescent lamp. This is of importance in the dyeing and printing of textiles, since it is unnecessary to treat the salts with hydrochloric acid to form diazonium salts and to couple these with alkaline β-naphthol or other phenols, or with a base, but only to expose the solutions with the other azo- component to heat, sunlight or ultraviolet light. It may also be of importance in negative diazo-printing. It was found possible with the halogenated bases easily to reproduce not only the image of any object impenetrable to sunlight, but also the colored image of the negative obtained by the ordinary photographic process.[237] The effect is not observed with *o*-toluidine, 1,3,4-xylidine, pseudocumidine and mesidine. Acidification of the alkaline coupling solution of diazotized aniline and acetamide gave a colorless precipitate which when dried rapidly in darkness was found to have the composition and molecular weight of acetylphenyltriazene. The crystals became reddish yellow in diffused light and after two weeks were a beautiful dark red. During this process the melting point dropped from 101 to 96°C.[238]

Cloth treated with certain vat dyes and dried may also be printed under a negative until the desired oxidation is complete, after which the unoxidized portion of the dye is removed by a boiling soap solution.[239] The dyes sensitive to ultraviolet include Indigosol Orange HR, Scarlet HR and Pink HR. Indigosol 4B and HB are less sensitive to sunlight.

PHOTOGRAPHIC PAPERS

In obtaining photographic images, Gay[240] mixed light-sensitive diazo- compounds with O-acyl derivatives of the phenols or naphthols, used as coupling components in development. The phenols or naphthols are liberated by development with ammonia gas or a dilute alkaline bath and a colored positive image is obtained.

For diazotypes, Kalle & Co.[241] use a diazo- compound capable of self-coupling in alkaline media applied in neutral or acid solution to the support. After exposure under a positive, the print is developed with gaseous ammonia. Suitable diazo- compounds are those from H-acid, 3-amino-6-N-piperidinobenzoyl-H-acid and 2,7-aminonaphthol.

Spencer[242] states that diazo- compounds for photographic papers should be sufficiently sensitive to light, and stable toward heat, mechanical shock, and to the paper base upon which they may be coated in sufficient concentration by the use of an inert solvent. They should couple readily with amines and phenolic compounds to give dark-colored substances insoluble in water and stable to light. The decomposition products should not interfere with the color or stability of the image. The following types of paper are possible: (a) the diazo- compound is decomposed by light and is developed by application of an alkaline coupler which reacts only with the unchanged diazo- compounds; (b) the diazo- compound and coupler are coated together, but reaction is prevented by the presence of an organic acid, such papers being developed by weak alkali solutions or ammonia vapor; (c) the diazo- compound is coated with a coupler in an unreactive state, *e.g.*, as an additive compound, development being effected by breaking up the additive compound by heat, ammonia, etc.; (d) the diazo- compound is decomposed by light into a substance which will react with the original diazo- compound either on keeping or in the presence of alkali.

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[237] Oddo, G., and Indovina, R., *Gazz chim ital.*, **65**, 1037, 1099 (1935); *Chem. Abs.*, **30**, 4830 (1936).

[238] Oddo, G., and Algerino, A., *Ber*, **69B**, 279 (1936); *Chem. Abs.*, **30**, 3418 (1936). For a discussion of visible light effects in certain phenyldibenzoxanthrenium dyes, see Dilthey, W., and Quint, F., *Ber.*, **69B**, 1575 (1936).

[239] Cowper, W., *Dyer, Calico Printer*, **58**, 117 (1927); *Chem. Abs.*, **22**, 1045 (1928).

[240] Gay, E., British P. 282,894 and 283,274 (1926); *Brit. Chem. Abs.*, **B**, 173 (1928).

[241] British P. 297,363, Aug. 19, 1928, to Kalle and Co.; *Brit. Chem. Abs.*, **B**, 350 (1930)

[242] Spencer, D. A., *Phot. J.*, **68**, 490 (1928); *Brit. Chem. Abs.*, **B**, 73 (1929).

A combination of boric acid and an organic acid (citric, tartaric) is more efficient than the organic acid alone in preventing the premature formation of coloring matters in diazo- papers in which the coupling agent and the diazo- compound are applied together.[243] A suitable coating mixture is: stannic chloride double salt of 4-diazo-1-dimethylaniline, 22, boric acid, 20, tartaric acid, 50, phloroglucinol 2 and water 1000 parts. Preservation by depriving the surface of moisture during the preparation is also described.[244]

Neuroth[245] prepared light-sensitive layers by bringing aryl azides onto a support together with phenols, aromatic amines or aminophenols. Development of the exposed layer is effected by washing out the unreacted azide or by rendering it inactive by reduction.[246]

Schmidt and Spietschka[247] described the manufacture of light-sensitive paper from diazo- compounds of aminonaphtholcarboxylic acids, such as 1-diazo-2-hydroxy-3-naphthoic acid in sodium hydroxide. If exposed beneath a negative and washed with water, a blue-black print on a pure white ground is obtained. Schmidt and Zahn[248] add a compound other than a dye showing strong ultraviolet absorption, as sodium 6-phenyl-2-aminopseudo aziminobenzene-3,4′-disulfonate, to inks, or crayons for making drawings from which blue prints are to be prepared, in order to secure clearer reproduction.

Miscellaneous Processes. In a photographic method for the reproduction of natural wood grains, the softer parts of the wood are removed by chemical and mechanical means. The pattern is then fixed on a photographic plate from which the printing surface is produced. The treated wood may be illuminated by ultraviolet light for reproduction or may be directly printed by x-rays.[249]

Beebe[250] described a compound adapted for reproducing designs on metal, glass, etc. which comprises a varnish containing a light-sensitive oil (tung) and an accelerator (iodine) which serves to accelerate the action of light on the varnish for photographic purposes.

On the assumption that cellulose products as ethers or esters, papers, artificial soaps, etc., on exposure to ultraviolet light become permeable to gases, vapors or liquids, Kleiner,[251] patented a method for the production and reproduction of pictures or designs by visible or invisible rays.

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[243] British P. 294,247, July 16, 1928, to Kalle & Co.; *Brit. Chem. Abs.*, **B**, 1033 (1929).

[244] N. V. Phillips' Gloeilampenfabrieken. French P. 794,590, Feb. 20, 1936; *Chem. Abs.*, **30**, 5137 (1936).

[245] Neuroth, H., German P. 510,165, Oct. 22, 1929, to Kalle & Co; *Chem. Abs.*, **25**, 886 (1931).

[246] See also Werner, G, U. S. P. 2,063,832; *Chem. Abs.*, **31**, 620 (1937); Alink, R., U. S. P. 2,083,285; *Chem. Abs.*, **31**, 5285 (1937).

[247] Schmidt, M. P., and Spietschka, W., German P. 470,088, Dec. 11, 1927, to Kalle & Co.; *Chem. Abs.*, **25**, 466 (1931).

[248] Schmidt, M. P., and Zahn, R., German P. 517,159, July 24, 1926, to Kalle & Co.; *Chem. Abs.*, **25**, 2066 (1931).

[249] British P. 308,373-4-5-6, March 22, 1928, to Masa G.m.b.H. zur Herstellung künstlicher Oberfläche; *Chem. Abs.*, **24**, 32 (1930). See also for another process, R. R. Tanner, U. S. P. 2,127,944, Aug. 23, 1938; *Chem. Abs*, **32**, 7840 (1932).

[250] Beebe, M. C., U. S. P. 1,574,356-7-8-9, Feb. 23, 1926; *Chem. Abs.*, **20**, 1362 (1926).

[251] Kleiner, S., British P. 413,095, April 26, 1933; *Chem. Abs*, **29**, 417 (1935).

Polden[252] employs light or ultraviolet radiations or electric currents at superatmospheric pressures to accelerate the bleaching of tortoise shell and similar natural materials by bleaching agents that yield nascent oxygen, such as hydrogen peroxide.

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[252] Polden, D. C., British P. 429,524, May 31, 1935; *Chem. Abs.*, **29**, 7531 (1935).

Chapter 33

Miscellaneous Applications of Ultraviolet Light

An application of the polymerization of oils by ultraviolet light is to be found in the production of patent leather. It has been claimed that the exposure of the varnished surfaces to the action of a mercury-vapor lamp gives the same result in one and one-half hours as is obtained by several days of exposure to sunlight. The method is not, however, widely used.

One process is carried out in an atmosphere containing ammonia derivatives, nitrogen, hydrogen or other neutral gases,[1] or in an exhausted chamber. The leather is carried on frames in the chamber, quartz lamps being arranged between the frames.[2] Lumbard[3] claims that better results are obtained if the extreme ultraviolet rays are filtered out.

An apparatus for the treatment described by Priest,[4] comprises a frame arranged on bearings which serves as a support for the hides which are to have their varnished surfaces exposed to the direct action of the ultraviolet rays. The action of the rays from a series of quartz lamps vertically arranged in the center of the revolving frame may be supplemented by the action of ozone.

Stoeckly[5] used ultraviolet rays produced by a high-frequency spark discharging thirty to sixty times per second, each spark consuming about 0.7 kilowatt. Prior to the use of artificial ultraviolet sources, the stock coated with the linseed oil varnish mixture was exposed to the direct rays of the sun for eight to ten hours. Such drying was greatly retarded by a humid atmosphere. Dinsley and Pulman[6] suggested subjecting leather to the ultraviolet rays prior to enameling it. Other patents dealing with structural features of the apparatus employed are due to Hughes,[7] and to Elliott[8]

The kind of plasticizer is of primary importance in determining the rate of deterioration of nitrocellulose films in artificial leather if embrittlement and insolubilization of the surface on exposure to light are to be avoided.[9] Anderson and Lamb[10] studied the properties of films containing various plasticizers, added to the extent of 0.25 to 2.0 per cent to films from a 3-per cent solution of Cotton 8A (nitrocellulose) in equal parts of butyl acetate and butyl alcohol. The films were formed by flowing on glass and exposing to the mercury arc. Of the eight plasticizers studied, "Sipaline AOM" (dimethylcyclohexyl adipate) gave the best results as regards flexibility and durability on exposure to ultraviolet light. Triacetin is also recommended for leather which requires much stretching.

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[1] Heyl, C., British P. 113,622, Feb 21, 1918; Swiss P. 76,436, Dec 17, 1917, British P. 113,620, Feb. 20, 1918.

[2] See also Swiss P. 77,117 and 77,378; Dutch P. 1,970; Danish P. 22,258 and 22,269; Hintz, E., *J. Soc. Chem. Ind.*, **37**, 709A (1918), *Chem Abs.*, **12**, 1935 (1918); U S. P. 1,269,931, June 18, 1918

[3] Lumbard, V. G., *J. Am. Leather Chem. Assn.*, **10**, 86 (1915); *cf.* Lattey, W. T., *J. Oil and Colour Chem. Assoc.*, **9**, 45 (1926); *Brit Chem. Abs*, **B**, 377 (1926).

[4] Priest, G. W., U S. P. 1,262,977, April 16, 1918; *J. Soc. Chem. Ind.*, **37**, 343A (1918).

[5] Stoeckly, J. J., British P. 148,454 and 149,334, 1920; *Chem. Abs.*, **15**, 329, 450 (1921).

[6] Dinsley, A., and Pulman, A O, British P. 190,781, Sept. 23, 1921; *J. Soc. Chem. Ind.*, **42**, 193A (1923).

[7] Hughes, W. A., U. S P. 1,747,301, Feb. 18, 1930, to Cooper-Hewitt Electric Co.

[8] Elliott, E L, U. S. P. 1,702,043, Feb. 12, 1929, see also Brophy, J J., U. S P. 2,020,296, British P. 452,618, Oct. 26, 1935; *Brit Chem. Abs*, **B**, 1109 (1936).

[9] Genin, G., *Halle aux cuirs*, 67, (1932); *Chem. Abs.*, **26**, 3136 (1932).

[10] Anderson, H., and Lamb, M. C., *Cuir tech.*, **23**, 130 (1934); *Chem. Abs.*, **28**, 5999 (1934).

Ultraviolet rays shorter than 3000A rapidly darken leather. This property can be used to produce designs on leather by the aid of stencils or Uviol glass photographic plates.[11] The darkening is caused by an iron-tannin compound. Light activates or frees both tannin and iron. Inorganic or organic compounds can be used to increase the depth and permanency of the designs or to alter their shade.

All vegetable-tanned leathers darken on exposure to light, frequently with a loss of strength, but [12] this is most marked in leathers tanned with catechol tannin. Attempts to find an effective inhibitor have been unsuccessful. The presence of water is necessary for darkening in ultraviolet light.

Fluorescence analysis methods have found application in leather chemistry.[13] Cuccudoro [14] believed it possible by such methods to assist in distinguishing between the various components of raw hide, that is, collagen, keratin, bloody tissues, and tanning materials. They also were found useful in determining the depth of penetration of vegetable tannins and the saturation of the hides with such materials and also in the examination of finished leather for indications as to the manufacturing processes which had been employed.[15]

The absorption spectra of solutions of various tanning materials have been measured by de la Bruère.[16]

The use of the ultraviolet microscope, which combines increased resolving power with the advantages of fluorescence, is finding application in the study of animal skin.[17]

PETROLEUM PRODUCTS

Absorption Studies. Crude petroleum oils are characterized by absorption bands with maxima at about 3000, 2800, 2650, 2420 and 2400A due probably to cyclic hydrocarbons [18] Transformer oils of various origins cannot be distinguished by ultraviolet absorption spectra. Aging of the oils merely decreases the sharpness of the bands.[19] It has been stated that benzene, xylene and toluene can be readily determined in gasoline by ultraviolet absorption studies Relatively little has, however, been written regarding the absorption of light by various petroleum products.[20] Schou and Bendix-Neilsen [21] find the absorption of a band at 2730A in samples of liquid paraffin parallels the results of the sulfuric acid test for organic impurities.

Mineral oils dissolved in various solvents change color on exposure to light according to the nature of the solvent.[22] Carbon tetrachloride, chloroform and amyl alcohol are the most active, but no changes take place in acetone and ether. In the absence of air, the discoloration is probably due to soluble polymerization products.

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[11] Freytag, H., *Collegium,* 161, (**1932**); *Chem. Abs.,* **26,** 3955 (1932), French P. 707,490.

[12] Woodroffe, D, *J. Internat. Soc. Leather Trades Chem.,* **18,** 424 (1934); *Chem. Abs.,* **28,** 6340 (1934).

[13] Deforge, A., *Halle aux cuirs,* 36, 83 (**1928**); Grasse, G., *Cuir tech.,* **20,** 141 (1931).

[14] Cuccudoro, M., *Boll. ufficiale staz sper. ind. pelli mat. concianti,* **10,** 237 (1932); *Chem. Abs.,* **27,** 624 (1933).

[15] Further reviews of these methods have been given by Desmurs, G., *Cuir tech.,* **21,** 40, 57, 77 (1932), Karsten, A., *Ledertech. Rundschau,* **26,** 93 (1934), *Cuir tech.,* **23,** 330 (1934); **24,** 36 (1935); **24,** 198 (1935). Karsten described a fluorescence microscope for use in the leather industry.

[16] de la Bruère, A., *J. Soc. Leather Trades Chem.,* **9,** 427 (1925); *Chem. Abs.,* **19,** 3384 (1925); Deforge, A., *Halle aux Cuirs,* 131 (**1929**).

[17] Theis, E. R., and Serfass, E. J, *J. Am. Leather Chem. Assoc.,* **33,** 67 (1938).

[18] Vlès, F., and Gex, M., *Compt. rend.,* **180,** 140 (1925).

[19] Vellinger, E., and Klinkenberg, A., *Ann. combustibles liquides,* **10,** 79 (1935); *Chem. Abs.,* **29,** 1815 (1935).

[20] Luszczak, A., *Abhandl. Gesamtgebiete Hyg. No.* **22,** 59 (1926); *Chem. Abs,* **31,** 4801 (1937) Certain photochemical reactions of Russian petroleum have been discussed by Pyhälä, E., *Mat. grasses,* **23,** 9124, 9182 (1931).

[21] Schou, S. A., and Bendix-Nielsen, I. B., *Dansk Tidskr. Farm.,* **4,** 1 (1930); *Brit. Chem. Abs.,* **B,** 263 (1930); *Arch. Pharm.,* **272,** 761 (1934); *Chem. Abs,* **29,** 915 (1935).

[22] Vellinger, E., and Marchand, P., *Ann. combustibles liquides,* **5,** 977 (1930); *Chem. Abs.,* **25,** 4391 (1931); Vellinger, E., *Ann. combustibles liquides,* **12,** 195, 250 (1937); *Chem. Abs.,* **31,** 7629 (1937).

With air, the change in color is not as distinctive, but insoluble oxidation products are formed. Shile and Avakova [23] find paraffin containing more than 0.1 per cent of oil to be unstable toward ultraviolet rays. Such paraffin, treated with fullers' earth and exposed to ultraviolet rays, is light-stable.

Heavy liquid pharmaceutical petrolatums of different geographical origins differ considerably in resistance to spoiling by exposure to sunlight in flint glass bottles.[24] The light-stability can be measured by comparatively short exposures of the oil in flint bottles to ultraviolet light.

It was once suggested that ultraviolet light be employed in the cracking of petroleum oils. They were to be heated with a catalyst and sprayed through an irradiated zone.[25] A patent to Physical Chemistry Research Co.[26] described the preparation of liquid hydrocarbons suitable for use as fuels by distilling solid fuels and subjecting the resulting gases, together with carbon monoxide and hydrogen, to the action of both ultraviolet rays and a high-potential electrostatic field.

Egloff [27] heats normally incombustible hydrocarbon gases from oil-cracking under superatmospheric pressure to about 650 to 1000°C., then lowers the pressure on the gases and subjects them to the action of ultraviolet light..[28]

Miller [29] renders solar light petroleum distillates, refined by treatment with silica gel, sweet to the "doctor test" by exposure to the radiations from a mercury-vapor lamp. Morrell [30] treats hydrocarbon distillates containing mercaptans by converting them to mercaptides by treatment with "Sunlite" solutions and then precipitates the mercaptides by exposing the products to ultraviolet light.

The bloom or fluorescence of petroleum oil may be destroyed by ultraviolet rays.[31] Some oils are thereby reddened in color or otherwise slightly darkened. Other oils are bleached by such treatment. Petroleum oils intended for use as lubricants and which may have gumming properties due to unsaturated components are improved in quality by exposure to ultraviolet rays in an inert gas. Apparently polymerization occurs, resulting in the formation of saturated bodies. Gray [32] deblooms lubricating oil, paraffin wax and the like and brings about partial conversion to acids and esters by blowing air through the hydrocarbon material at 50 to 120°C., while exposing it to ultraviolet rays. Catalysts may be present and the operation may take place at pressures up to five atmospheres. Gray states that he has been able to convert 75 per cent of the hydrocarbon material into fatty acids by this process.

Color Changes. Gasolines refined from certain California crude oils not treated by clay or acid tend to take on a color which may be pink, yellow or light chocolate when the product is dispensed in a visible pump in the presence of sunlight. McConnell [33] proposed to treat such oils by exposing them to daylight for fifteen to thirty or more daylight hours to fix the color or complete the color reaction to its maximum and then remove the discoloring compound, preferably by distillation. In this process, the sensitive portion, which is probably an organic sulfur compound, is rendered non-volatile and remains in the residue on distillation. The distillate then retains its freedom from color on exposure to sunlight. The process is known as complete fixation. It is said that the process may also be applied to the first pressure distillate of cracked gasoline and so obviate the necessity of treating a large percentage of the cracked gasoline with either acid or clay.

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[23] Shile, V. N., and Avakova, E. S., *Nestyanoe Khozyaistvo,* **25,** No. 9, 59 (1933), *Chem. Abs.,* **28,** 4886 (1934).

[24] Green, L. W., and Schoetzow, R. E., *J. Am. Pharm. Assoc.,* **21,** 1286 (1932); *Chem. Abs ,* **27,** 1987 (1933).

[25] French P. 469,948, 1914, to Continental Caoutchouc and Gutta-Percha Co.

[26] British P. 357,206, June 4, 1929, to Physical Chemistry Research Co.; *Chem. Abs.,* **26,** 4701 (1932).

[27] Egloff, G., U. S. P. 1,904,362, April 18, 1933, *Brit. Chem Abs.,* **B,** 134 (1934).

[28] For a patent relating to the utilization of ultraviolet rays for supporting combustion in heat engines, see Gill, H. A., British P. 269, 808, Nov. 9, 1926.

[29] Miller, E. B., U. S. P. 1,647,459, Nov. 1, 1928; *Chem. Abs.,* **22,** 315 (1928).

[30] Morrell, J. C., U. S. P. 1,904,382, April 18, 1933, to Universal Oil Products Co.; *Chem. Abs.,* **27,** 3601 (1933).

[31] Ellis, Carleton, U. S. P. 1,089,359, March 3, 1914.

[32] Gray, T. T., U. S. P. 1,158,205, Oct. 26, 1915.

[33] McConnell, J. R., U. S. P., 1,590,841; June 29, 1926; *Chem. Abs.,* **20,** 3077 (1926).

Even paraffin has been improved in its fastness to light by treating it with decolorizing agents and radiations of short wave-lengths together or in turn. Oxygen may be supplied during the irradiation.[34]

Kovalev and Illarionov [35] exposed Grozny petroleum distillates to sunlight for three months with free access of air. Kerosene, light and heavy solar oil, spindle oil, engine oil and cylinder oil were used. The specific gravity and refractive indices of the samples changed very little. The dielectric constant increased at first, but after two months decreased. The drop in the third month is explained by supposing that rearrangement takes place in an oxygen compound, the added active oxygen being given to other unsaturated molecules forming ketoxy and oxy-compounds. No aldehydes were found. Panchenkov and Puzitsckiĭ,[36] however, state that certain wave-lengths increase the viscosity of lubricating oils.

In testing the color stability of gasoline to sunlight, Hoeman [37] used a ferric oxalate actinometer for gauging the intensity of the sunlight at the time the test exposures on the gasoline are made Lowry, Smith and Murphy [38] standardized a carbon arc source against the summer sun in testing the color change in gasolines. The samples were exposed in 4-oz. oil bottles of ordinary glass, Corex glass and quartz. It was found that a West Texas gasoline, when exposed in glass to a cerium-containing carbon arc, changed in color from Saybolt 22° to 17° in ten minutes. Another listed as "commercial gasoline B" changed from 23° to 17° in thirty minutes.

A study of the way in which some gasolines become hazy and discolored and deposit sediment in a glass dispensing bowl has been made by Morrell, Benedict and Egloff.[39] In reviewing earlier work,[40] they state that it had been indicated that color formation in gasolines is due to oxidation reactions involving sulfur compounds or unsaturated hydrocarbons. Samples of Midcontinent straight-run gasolines, cracked gasoline and a blend of equal parts of straight-run and cracked gasoline were exposed in quartz cylinders for an hour to a carbon arc in the presence of air, oxygen, nitrogen, carbon dioxide or hydrogen. In the presence of air or oxygen, all samples developed color, gum, peroxides, acids and aldehydes. Although the straight-run and blended gasolines developed haze, the cracked ones did not. Cracked and blended gasolines developed more gum in oxygen than did straight-run gasolines. Under inert gases, the straight-run gasoline dropped in color from 30° to 28° only, and the cracked and blended gasolines were unaffected. There was no formation of acid or gums and only very small amounts of peroxides.

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[34] German P. 475,343, Aug. 28, 1926, to Werschen-Weisserfelser Braunkohlen, A. G.; *Chem. Abs.*, **23**, 3341 (1929). See also[22].

[35] Kovalev, T. G., and Illarionov, V. V., *J. prakt. Chem.*, **138**, 306 (1933); *Chem. Abs*, **28**, 1513 (1934).

[36] Panchenkov, G. M., and Puzitsckii, K W., *J. Gen. Chem. (U.S S.R.)*, **7**, 394 (1937); *Chem. Abs.*, **31**, 4800 (1937).

[37] Hoeman, E. C., *Oil and Gas J.*, **32**, No. 17, 18 (1933); *Chem Abs*, **27**, 5525 (1933).

[38] Lowry, C. D., Jr., Smith, M. A., and Murphy, G. B., *Ind. Eng. Chem. (Anal. Ed.)*, **7**, 140 (1935).

[39] Morrell, J. C., Benedict, W. L., and Egloff, G., *Ind. Eng. Chem.*, **28**, 122 (1936); Egloff, G., Morrell, J. C., Benedict, W. L., and Wirth, C., *Ind. Eng. Chem.*, **27**, 323 (1935).

[40] Brooks, B. T., *Ind. Eng. Chem.*, **18**, 1203 (1926); Brooks, B T., and Parker, H. O., *Petroleum*, July 14, 1924; Carpenter, J. A., *J. Inst. Petroleum Tech.*, **12**, 518 (1926); *Chem. Abs.*, **21**, 1702 (1927).

The addition of sulfur (0.01 to 0.1 per cent) was deleterious either in the presence or absence of oxygen. With air or oxygen, it caused a marked increase in the amounts of color and gum formed. The acid formation and peroxide number were also greater than in the absence of added sulfur. With added sulfur, the color depreciation and gum formation were less in the absence of oxygen, no haze or acids appearing and only very small amounts of peroxides developing. Hydrogen sulfide was evolved in all cases. Oxygen is necessary for the formation of haze, acids or peroxides, but not always for the formation of gum or color. The elemental sulfur was almost completely removed as such during exposures either with or without oxygen. Oxides of sulfur were formed.

The addition of *n*-propyl disulfide (representative of disulfides likely to be present in gasolines or formed by sweetening) decreased the color stabilities in light and air of straight-run and blended gasolines. The decreases were greater in oxygen and even the cracked gasoline was affected. The disulfide had, however, no effect on the gum formation in gasolines exposed to air, although in those exposed to oxygen it caused a small increase. The peroxide number of the straight-run gasoline was lower and the acid number higher than in the absence of added disulfide. This was not, however, true of the cracked gasoline. Disulfide addition caused no depreciation of gasolines exposed in hydrogen, nitrogen or carbon dioxide. Mercaptans were formed during exposures in non-oxidizing atmospheres.

No fixed relation was found between color and gum formation. They can form simultaneously or gum can form with no color depreciation; or color can form without an increase in the gum content. Haze particles contain sulfur dioxide and trioxide or the corresponding acids and organic material. Most of the acid formed in gasoline was found in the haze particles which could be removed by filtration through filter paper. Although this improved the color, it did not affect the gum content of the gasoline.

Results obtained with Pennsylvania and California gasolines were similar, with the following exceptions. The Pennsylvania straight-run gasolines with no added sulfur compounds did not form gum on exposure to light and air, although gum was formed in oxygen. The addition of *n* propyl disulfide caused slight increases in gum formation in the Pennsylvania cracked gasoline and in all of the California gasolines. The results with the inert atmospheres were the same as with the Mid-continent gasolines.

These workers have again recently emphasized that color is formed only in the presence of sulfur or *n*-propyl disulfide.[41]

Pure hydrocarbons exposed to the carbon arc under oxygen give traces of peroxides, acids and aldehydes. The bromine number and refractive index are unchanged by light, either in the presence or absence of sulfur and propyl disulfid.[42]

Vellinger and Radulesco[43] exposed samples of motor fuels under oxygen in closed Pyrex containers to the rays of a mercury lamp and found the amount of gummy material formed to be a function of the rate of absorption of oxygen. At the beginning, the quantity of gum formed was almost proportional to the amount of oxygen absorbed. Gradually, however, the absorption of oxygen diminished and approached a limit set by the particular pretreatment to which the sample had been subjected.

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[41] Morrell, J. C., Benedict, W. L., and Egloff, G., *Ind. Eng. Chem.*, **28**, 122, 448 (1936).

[42] Note also Berger, G. W., *Refiner Natural Gasoline Mfr.*, **15**, 411 (1936).

[43] Vellinger, E., and Radulesco, G., *Compt. rend.*, **196**, 1495 (1933); *Ann. combustibles liquides*, **8**, 883 (1933); *Chem. Abs.*, **28**, 621 (1934).

On the other hand, Freund[44] believed the absorption of oxygen of secondary importance. He considered the resins to be formed from complicated unsaturated hydrocarbons. A brief irradiation resinified only the most unstable unsaturated compounds. The resinous, gum-forming compounds produced in petroleum-cracked products by ultraviolet rays increased in amount with the exposure. Extremely small amounts were formed in comparison in primary benzines, paraffins, naphthenes and aromatic and simple unsaturated hydrocarbons. It was found that sulfur and oxygen compounds were almost completely removed from the benzines during separation of the resin.[45]

The larger the storage tank, the slower the diffusion of oxygen and the less the gum formation. Sunlight lowers the induction period for gum formation, but water has the opposite effect. The rate of gum formation roughly triples for every twenty degrees rise in temperature.[46]

To stabilize cracked distillates, especially from California or asphaltic base crudes, which contain more unsaturated and unstable constituents and more gum and coloring matter than the straight-run distillates from the same sources, Davis[47] employed a photochemical reaction. Daylight, sunlight or artificial ultraviolet sources were used and the undesirable constituents were oxidized in the presence of copper oxide. They formed organic acids which produced copper salts soluble in the oil and removed from it by subsequent distillation. A continuous stream of hydrocarbons in the vapor state mixed with oxygen can also be conveyed past a source of ultraviolet light and the oxidized products condensed, according to Martin[48]

Tauss[49] proposed to remove the resin-forming constituents in the refining of hydrocarbon oils by accelerating their polymerization by treating the hot oil or its vapor with very small amounts of oxygen and then removing the polymerization products. Other means could be used also, such as a glow discharge, irradiation or the addition of small amounts of acid or alkalies.

By a similar method, Goltstein[50] polymerized constituents in petroleum and similar hydrocarbons, thereby changing the physical characteristics of the distillate. By using an immersed quartz mercury-vapor lamp, at 60 volts and 6 amperes, the viscosity (Engler) of Russian mineral oil was increased from 6.4 to 7.8 in a half hour. The treatment may be applied to either the liquid or to the vapor phase during distillation.

In the cracking and distillation patent of Tingley,[51] the oil is subjected to the action of emanations from a radioactive substance or to ultraviolet rays before it enters a conduit within the furnace of the apparatus.

Light-stability may also be increased in cracked gasoline by the addition of 0.01 to 0.5 per cent of triacetoxytriethanolamine or other esters of the general formula $(RCOOR')_nNH$, in which R′ is aliphatic, R aliphatic or aromatic, x is 0, 1 or 2 and n 1, 2 or 3.[52]

Testing of Gasolines. The stability of gasolines may be tested by ultraviolet light in order to predict the tendency of the samples to form gums. Allusion to this appeared in a patent of Somerville and Hoffert.[53] Some have stated that the action of ultraviolet light is too severe as it resinifies certain compounds which remain stable on prolonged storage.[54] As a result the conclusions of such accelerated tests are not always in agreement with those obtained after storage for nine months. Nevertheless, the method has been frequently proposed. Beard and Reiff [55] standardize the radiations employed by their effect on an oxalic acid-uranyl acetate actinometer, and consider the effects of temperature. They note that discoloration started under radiation increases in darkness, which suggests a chain process. Schulze and Frey [56] exposed the fuel to actinic light rays while treating it with an aqueous solution of glycol and water as a separate liquid phase.

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[44] Freund, M., *Brenastoff-Chem.*, **14**, 61 (1933); *Chem. Abs.*, **27**, 3808 (1933)

[45] Freund, M., see also *Proc. World's Petroleum Congress*, **2**, 108 (1933); *J. Inst. Petroleum Tech.*, 83A, (**1934**); Balada, A., *Petroleum Z.*, **31**, No. 48, 11 (1933).

[46] McNamara, T. L., *Refiner and Natural Gasoline Mfgr.*, **13**, 381; *Chem. Abs.*, **29**, 2721 (1935).

[47] Davis, R. F., U. S. P. 1,551,806, Sept 1, 1925.

[48] Martin, R. B., U. S. P. 1,678,403, July 24, 1928, to Mineral Separations N. Am. Corp.; *Brit. Chem. Abs.*, **B**, 702 (1928).

[49] Tauss, J., German P. 475,277, Dec. 1, 1923; *Chem. Abs.*, **23**, 3340 (1929).

[50] Goltstein, E., British P. 249,895, Sept. 30, 1924; *Chem. Abs.*, **21**, 1007 (1927).

[51] Tingley, S. L., U. S. P. 1,627,937-8, May 19, 1927; *Brit. Chem. Abs.*, **B**, 516 (1927).

[52] Mikeska, L. A., and Holtzclaw, J. B., U. S. P. 2,110,274, March 8, 1938; *Chem. Abs.*, **32**, 3600 (1938).

Woog, Givaudon and Dacheux [57] found that the use of white light in tests for potential gum gave unsatisfactory results. The effect of ultraviolet light was determined by exposing the sample, first in crystallizing dishes covered with Cellophane and later in Pyrex glass to a quartz mercury arc (5.4 amp., 110 volts) at about 30 cm. The results were very decisive and revealed a difference in the quality of two gasolines between which bomb tests had failed to show a difference. The tests were completed by bomb tests following the irradiation Sufficiently reproducible results could be obtained when the gum did not exceed 10 mg. For higher values, the accuracy dropped to 10 per cent. The optimum conditions were thought to be ultraviolet treatment for one hour and heating at 100°C. for three hours. For ordinary gasoline, ultraviolet treatment for thirty minutes and heating for two hours sufficed.

Freund [58] found the results obtained by ten minutes of ultraviolet irradiation agreed closely with those of storage tests. The elementary composition of the gum so formed appeared to be the same as that formed during storage in darkness or under the influence of oxygen.

Baxter [59] observed gum formation in samples of gasoline derived from Colorado shale oil when treated in the presence of oxygen with sunlight, ultraviolet light or x-rays. Birch and Stansfield [60] found that samples of cyclohexane gave 0.2 gm. of peroxide oxygen per liter in a sample kept in light for six months and only 0.009 gm. per liter in a sample kept in darkness. No visible gum, however, deposited in the light sample. Cyclohexane in contact with air shows indications of the presence of peroxides after a short exposure to ultraviolet light.

In a patent of Rosenstein and Hund [61] on the addition of selenomercaptan to produce antiknocking gasolines, it was stated that untreated gasolines containing 62.2 mg. of gum per 100 cc. had after exposure to ultraviolet light for 24 hours a gum content of 102.9 mg. per 100 cc.. Selenomercaptan-treated samples had 33.5 mg. per 100 cc. before and 33.7 mg. after a similar irradiation. It was believed that this treatment with selenomercaptan checks the tendency to gum formation and may render unnecessary any previous fixation process for the removal of unsaturated materials.

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[53] Somerville, P. G., and Hoffert, W. H., British P. 289,347, Oct. 27, 1926; *Chem. Abs.*, **23**, 689 (1929).

[54] Brunschwig, R., *Chal. et ind.*, 315, Oct., 1928; *Brit. Chem. Abs.*, **1929B**, 931; Brunschwig, R., and Jacqué, L., *Compt. rend.*, **189**, 486 (1929).

[55] Beard, L. C., Jr., and Reiff, O. M., *Ind. Eng. Chem. (Anal. Ed.)*, **3**, 280 (1931).

[56] Schulze, W. A., and Frey, F. E., U. S. P. 1,950,697, March 12, 1934, to Philips Petroleum Co.; *Chem. Abs.*, **28**, 3562 (1934).

[57] Woog, P., Givaudon, J., and Dacheux, P., *Rev. petrolifere, No.* **584**, 721 (1934); *Chem. Abs.*, **28**, 7502 (1934).

[58] Freund, M., *World Petroleum Congress, London, Proc.* **2**, 108 (1933); *Chem. Abs.*, **28**, 4879 (1934).

[59] Baxter, R. A., *Ind. Eng. Chem.*, **21**, 1096 (1929).

[60] Birch, S. F., and Stansfield, R., *Nature*, **123**, 490 (1929).

[61] Rosenstein, L., and Hund, W. J., U. S. P. 1,835,184, Dec. 8, 1931.

Lead tetraethyl in gasolines may be stabilized against light and water by a small amount of a water-soluble fluoride.[62] One of the drawbacks to the use of iron pentacarbonyl as an antiknock agent is its instability to sunlight. Irlin and Solodovnik[63] propose the use of dyes as stabilizers to avoid this.

Other Applications to Petroleum Products. Chlorinated hydrocarbons for dry-cleaning, such as perchloroethylene, trichloroethylene and tetrachloroethylene, may be made stable to light by the addition of small amounts of butyl oxide, chloride or tartrate, Tetralin or Decalin.[64] Mitscherling[65] claims the formation from gasoline of alcohols and ketones by the action of a rare-gas lamp, such as one containing argon or neon. The irradiation is conducted in the presence of an oxidizing agent, such as a perborate or percarbonate, and a metal compound, such as copper hydroxide, to increase the electrical conductivity of the hydrocarbon material.

Irradiation with violet or ultraviolet light, x-rays, cathode rays, etc. has been suggested by Herbsman[66] for the separation of the components of such dispersed systems as petroleum-water emulsions or foams.

DRUGS AND RELATED PRODUCTS

There have been a few who have claimed to increase the potency of drugs by the application of ultraviolet rays. Cunningham and Macbeth[67] add fluorescent substances, such as quinine sulfate, to the liquid under treatment, vaporize it through an atomizing nozzle, and subject the vapor to the action of ultraviolet rays. Abrahamowicz[68] has proposed to treat arnica, camomile, pine needles, coltsfoot, lime or elder blossoms or stinging nettles, while dry, with both x-rays and ultraviolet rays, before using them in cataplasms.

Such claims are not well substantiated. No widely used applications are known, other than to the production of vitamin D discussed in a subsequent chapter.

Instead, pharmacists have long realized that light, and particularly, the shorter wave-lengths, exerts a deleterious action upon many drug preparations. Elaborate studies, too detailed for inclusion here, on the extent to which this may occur have been conducted by Arny, Taub and Steinberg.[69] Their work was mainly directed to spectrophotometric determinations of the transmissions of various wave-lengths by the types of containers available on the American market. In general, from three to twelve times as much deterioration occurred in direct light as compared with diffused light About 15 per cent of the drugs and chemicals tested were light-sensitive. Amber glass gave the best protection from ultraviolet rays. Red-flashed glass and Corning Red were very effective but are expensive. Few reputed stabilizers gave satisfactory results, although tin compounds stabilized phenol and, as is well known, acetanilide stabilizes hydrogen peroxide.

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[62] Michel, J M., U. S P. 2,067,331, to I. G. Farbenind. A -G ; *Chem. Abs.*, **31**, 1603 (1937).

[63] Irlin, A. L., and Solodovnik, *Novosti Tekhniki, No. 26*, 20 (1936); *Chem. Abs.*, **31**, 2404 (1937).

[64] de Schacken, J. M. G., and Schmidt, M. E. A., French P. 794,878, Feb. 27, 1936; *Chem. Abs.*, **30**, 5430 (1936).

[65] Mitscherling, W. O , U. S. P 2,003,303, June 4, 1935; 2,003,898; *Chem. Abs.*, **29**, 4771, 4931 (1935).

[66] Herbsman, A. M , British P. 356,926, Aug. 27, 1930; U. S. P. 1,783,471; *Chem. Abs.*, **25**, 365 (1931).

[67] Cunningham, E. L., and Macbeth, H. F., U. S P. 1,659,085, Feb 14, 1928; *Chem. Abs.*, **22**, 1440 (1928).

[68] Abrahamowicz, J., British P. 455,914, 1936; *Chem. Abs.*, **31**, 2359 (1937).

[69] Arny, H. V., Taub, A., and Steinberg, A , *J. Am. Pharm. Assoc.*, **20**, 1014, 1153 (1931); *Chem. Abs.*, **26**, 1395 (1932); Arny, H. V., *Glass Packer*, **12**, 497 (1933), *Chem Abs.*, **27**, 5913 (1933); Brunner, K., *Pharm. Zentralhalle*, **77**, 696, 721, 756, 783 (1936); Husa, W. J., *Glass Container*, **7**, No. 12, 9 (1928); *Chem. Abs*, **23**, 236 (1929).

Eisenbrand[70] believes that for highly sensitive substances, violet manganese glass is best. For less sensitive drugs, brown iron glass will usually suffice.

Rojahn[71] gave data on a number of alkaloidal solutions and tinctures. An exposure of a year to sunlight reduced the strength of tincture of hydrastis about 25 per cent and of tincture of capsicum 35 per cent. The tinctures of aconite, areca, belladonna, granatum and strophanthus were relatively stable, the losses being under 5 per cent. Alkaloidal and alkaloidal salt solutions, after 24 hours irradiation by ultraviolet light, suffered losses up to 31.3 per cent (cinchonidine). Cocaine was least affected. The losses were 23.6 per cent in tincture of hydrastis, 35.1 per cent in tincture of capsicum and 28 per cent in tincture of areca. The optical rotation also was lessened. The color of tincture of capsicum was decreased by exposure to daylight. In the tinctures of granatum, hydrastis and areca, it was increased.

Tribromoethyl alcohol is very unstable in light.[72] An exception to the behavior of many pharmaceutical preparations is offered by the decolorized solution of iodine which, according to Merry,[73] should be kept in colorless glass containers exposed to sunlight.

The mydriatic action of homatropine hydrobromide is not decreased by exposure to ultraviolet light, according to Pittenger and Krantz.[74] On the other hand, Macht and Krantz,[75] found that ultraviolet rays produce a rapid deterioration of the tincture of digitalis.On prolonged exposure, a point is reached at which there are formed products of increased toxicity for both plants and animals. On further exposure, a secondary weakening in potency occurs. Ultraviolet and polarized visible light were said also to cause a decrease in the anesthetic action of some isomeric octyl alcohols.[76] Macht and Hill[77] were unable to detect any loss of the antiseptic or germicidal action of 1 : 500 solutions of Mercurochrome-220 after exposure to ultraviolet rays or to polarized visible light. Krantz and Carr[78] found that elixir of pepsin and rennin became less acid on irradiation, but samples stored in amber glass compared favorably after six weeks in direct light (supplemented by Alpine lamp irradiation for one-half hour each week) with fresh preparations.

The toxicity of quinine for infusoria is increased by ultraviolet irradiation of its solutions, provided the intensity is sufficient. If too great, however, the fluorescense is increased and the toxicity decreased.[79]

It has been noted[80] that finely ground pyrethrum powders lose most of their toxicity in a few days of exposure to summer sunlight and air. With finely ground derris, the loss was about half as rapid. A one-hour exposure to a mercury-vapor lamp was equal in detoxicating power to eight hours of July sunlight and was more constant and easily controlled. Extracts in petroleum distillates were exposed by Hoyer[81] in tight flint-glass bottles to sunlight and daylight for four months and at intervals tested for their toxic action on flies. Sprays prepared with an odorless base gained slightly in toxicity during the first four days, but a sample prepared in an ordinary petroleum distillate lost toxicity from the start. After the fourth day, all samples lost toxicity rapidly, the loss being 65 per cent at two months and 90 per cent at four months. The increase observed in some at the start may have been due to the formation of an unstable toxic substance. The sprays with odorless base became hazy within three hours and their amber color was gradually lost. Finally, a white precipitate settled out. The sample with the ordinary base remained clear but lost some of its color. Chemical assays did not give consistent results. Pearson[82] found that the substitution of some of the pyrethrum by pine oil retards some of the changes.

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[70] Eisenbrand, J., *Pharm. Ztg.*, **72**, 1275 (1927); **74**, 263 (1929); *Chem. Abs.*, **22**, 137 (1928); **23**, 2247 (1929).

[71] Rojahn, C. A., and Herzog, H , *Pharm Zentralh.*, **73**, 401 (1932); *Chem Abs*, **26**, 5173 (1932), Rojahn, C. A , and Haase, E., *Pharm. Zentralh.*, **74**, 625 (1933); *Chem. Abs*, **28**, 855 (1934).

[72] Fialkov, Y A., *Farm. Zhur.*, *No.* **3**, 184 (1937); *Chem Abs.*, **32**, 3905 (1938).

[73] Merry, J. J. F., *Pharm. J.*, **140**, 347 (1938); *Chem. Abs.*, **32**, 3909 (1938).

[74] *Pittenger, P. S., and Krantz, J. C., Jr , J. Am Pharm. Assoc.*, **17**, 1081 (1928); *Chem Abs*, **23**, 1214 (1929).

[75] Macht, D. I., and Krantz, J. C., Jr., Proc. Soc. Exptl. Biol. Med., **23**, 340 (1926); Macht, D. I., *Arch. Phys. Therapy, X-ray, Radium*, **13**, 5 (1932); *Chem Abs*, **26**, 1667 (1932).

[76] Schroeder, H., and Macht, D. I., *Arch exptl. Path. Pharmakol.*, **158**, 53 (1930); *Chem. Abs* **25**, 4049 (1931).

[77] Macht, D. I., and Hill, J. H., *J. Am Pharm. Assoc* , **16**, 110 (1927).

[78] Krantz, J. C., Jr., and Carr, C. J., *J Am Pharm. Assoc* , **19**, 32 (1930).

[79] Fedorov, B. T., *Bull. soc. naturalistes Moscou, Sect. biol.*, **44**, 119 (1935); *Chem. Abs* , **30**, 2643 (1936).

[80] Badertscher, A. E., and Wotherspoon, R., *Soap (Sanitary Products Section)*, **11**, No. 4; **87**, 111, 113 (1935); *Chem. Abs.*, **29**, 4125 (1935).

Fleming and Baker[83] found that exposure to ultraviolet light reduces the value of rotenone as a stomach poison for the Japanese beetle, although the value of derris and rotenone as repellants was but slightly reduced by exposure for 24 hours.

Prolonged sun-drying of pyrethrum caused appreciable losses, but quick drying in the sun did not.[84] According to Jones, Gersdorff, Gooden, Campbell and Sullivan,[85] the photochemical decomposition of dry rotenone does not take place in the absence of oxygen. Rotenone, its hydrochloride, rotenone-bentonite mixture, derris root and derris extract lost more than half their toxicity during a ten-day exposure to sunlight. Arc light practically destroyed their toxicity. Dihydrorotenone was more resistant, requiring twenty days in sunlight, but in arc light it lost toxicity to about the same extent as rotenone. Lampblack afforded some protection.

Anthelmintic capsules of tetrachloroethylene intended for animals, may be stabilized against light[86] by incorporating an oil-soluble red dye such as Oil Soluble Red O. Deichsel[87] uses 0.5 per cent of the azo- dye from *o*-anisidine and β-naphthol to make light-stable a solution comprising a terpene oxide such as ascaridol.

Tobacco. Ultraviolet light is occasionally applied to tobacco for the purpose of killing molds on the leaves. It has also been recommended for slightly altering the color. Dorcas[88] states that this may have important applications in foreign markets, but in the United States is not particularly important, except for leaves intended to serve as cigar wrappers. Exposure to ultraviolet also causes a number of little understood changes in the quality of the tobacco.

The Neuerburg'sche Verwaltungs Gesellschaft[89] claimed that the denicotinizing of tobacco by fermentation may be accelerated by irradiation with wave-lengths shorter than 4000A and that the application of ultraviolet light improves tobacco which has been tainted and partly degraded by mold and other micro-organisms. Richter[90] claimed to reduce the toxicity of cut or sliced tobacco by exposing it on an endless conveyor belt to ultraviolet, infrared or visible light of specified wave-lengths. Pacini[91] first dampened the tobacco with water containing a "sauce" which may contain coumarin, etc. and an agent such as glycerol, ethylene glycol, malic, or tartaric acid which was believed to counteract the opacity of the other constituents of the sauce, before irradiating it.

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[81] Hoyer, D. G., *Soap (Sanitary Products Section)*, **11**, No. 12, 105, 107, 109, 111 (1935); *Chem Abs.*, **30**, 786 (1936).

[82] Pearson, A. M., *Del Agr. Expt. Sta Bull.*, **196**, 5 (1935); *Chem. Abs.*, **30**, 3570 (1936).

[83] Fleming, W. E., and Baker, F. E., *J. Agr. Research*, **53**, 197 (1936); *Chem. Abs.*, **30**, 8497 (1936).

[84] Beckley, V. A., and McNaughton, F., *E. African Agr. J.*, **2**, 327 (1937); *Chem. Abs.*, **31**, 5503 (1937).

[85] Jones, H. A., Gersdorff, W. A., Gooden, E. L., Campbell, F. L., and Sullivan, W. N., *J. Econ. Entomol.*, **26**, 451 (1933); *Chem. Abs.*, **27**, 4015 (1933).

[86] Anderson, C. N., U. S. P. 1,703,377, Feb. 26, 1929, to Parke Davis and Co.; *Brit. Chem. Abs.*, **B**, 453 (1929).

[87] Deichsel, S., U. S. P. 2,066,717, to Winthrop Chemical Co.; *Chem. Abs.*, **31**, 1040 (1937).

[88] Dorcas, M. J., *Trans. Illum. Eng. Soc.*, **28**, No. 7, 575 (1933).

[89] German P. 507,194 and 527,361, 1928, to Neuerburg'sche Verwaltungs Gesellschaft; *Chem. Abs.*, **25**, 560, 4664 (1931). See, however, Chapter 27.

[90] Richter, C. M., British P. 359,920, May 3, 1929; *Chem. Abs.*, **26**, 4916 (1932).

Lilienfield[92] claimed the irradiation would render mild and cure, strong, previously aged and fermented tobacco leaves.

Chesley[93] subjects cured and aged tobacco to ultraviolet rays which constitute a selected portion of the light used. It is applied by special carbon arc lamps, the tobacco being continuously moved in a revolving drum to subject every part to the action of the rays without appreciably reducing the moisture content. There also was used a small proportion of infrared and visible radiation. Wix and Bunker[94] treat tobacco in a drum, part of the wall of which is of quartz, by a mercury arc.

In a curious method of preserving the aroma of tobacco, Senftner[95] incloses it in an envelope of cellulose material the pores of which are filled with ergosterol or cholesterol which may be irradiated.

Although the discussion (Chapter 27) of the irradiation of nicotine would indicate that the alkaloid cannot be destroyed in tobacco leaves by irradiation for a reasonable time, it has been claimed that the alkaloids in tobacco, tea, coffee, etc may be decomposed by irradiating the products in the presence of a 1.5-per cent sodium bicarbonate solution.[96]

Alcoholic Beverages. According to Henri, Helbronner and von Recklinghausen[97] wines may be quickly aged by ultraviolet irradiation. According to Petri,[98] exposure of wine to ultraviolet radiation for 0.6 to 4 seconds had no effect on the rate of fermentation, on the production of acids during maturation, or on the vitamin D content, but there may have been an insignificant increase in the content of vitamin C.

From time to time, it has been proposed to age whisky by ultraviolet light, but little or no application seems to have been made of such processes. Mancini and Archangel[99] would pass the rays into the whisky through quartz rods. The use of ultraviolet or infrared rays or a high-frequency or high-tension current in the aging of liquors is suggested by Stein[100] Merory[101] irradiates the vapors during distillation.[102] Philipsky[103] ages mead by irradiation. The non-aromatic constituents are removed and only the bouquet-producing extract is irradiated.

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[91] Pacini, A J., U. S P. 1,920,588, Aug 1, 1933, *Chem Abs.*, **27**, 4882 (1933).

[92] Lilienfield, W. E, U. S. P. 1,731,018, 1929, *Chem. Abs.*, **23**, 5547 (1929).

[93] Chesley, A. L, U. S. P. 1,926,035, 1933, to American Tobacco Co.; *Chem. Abs*, **27**, 5898 (1933), British P. 349,174, Feb. 21, 1930.

[94] Wix, A., and Bunker, S W., British P. 421,487, Dec 21, 1934; *Chem. Abs*, **29**, 3786 (1935).

[95] Senftner, G., U. S. P. 1,920,483, 1933, *Chem. Abs*, **27**, 4882 (1933)

[96] Popoff, M, German P 565,373, July 6, 1929; Kennedy, D. J., U S. P. 1,859,740, May 24, 1932 *Chem. Abs.*, **26**, 3857 (1932).

[97] Henri, V., Helbronner, A, and von Recklinghausen, M, U. S. P. 1,130,400, March 2, 1915.

[98] Petri, W., *Z. unters. Lebensm.*, **64**, 177 (1932); *Chem. Abs.*, **27**, 5469 (1933).

[99] Mancini, J., and Di Archangel, N. U. S. P. 2,040,264, 1936; *Chem. Abs.*, **30**, 4618 (1936); *Brit Chem. Abs.*, **B**, 487 (1937).

[100] Stein, J.-G., German P. 635,694, Oct. 4, 1936; *Chem Abs.*, **31**, 805 (1937).

[101] Merory, J., Austrian P. 149,188, April 10, 1937; *Chem. Abs.*, **31**, 5507 (1937).

[102] For the artificial aging of wines by ultraviolet light, note also Lord Investierungs-Korporation A. G., German P. 638,936, Nov. 25, 1936, 652,858, Nov. 10, 1937; French P. 807,371, Jan. 11, 1937 *Chem. Abs.*, **31**, 3204, 5508 (1937); British P. 468,990, July 16, 1937. A series of sublethal exposures at long intervals is used.

[103] Philipsky, A. J. H., German P. 557,806, March 18, 1933; *Chem. Abs.*, **27**, 559, 4343 (1933).

Miscellaneous Products

That exposure of a polished metal surface to ultraviolet rays may render it increasingly liable to corrosion was indicated by tests conducted at the Bureau of Standards.[104] Specimens of Armco iron, medium carbon steel, stainless steel, and high-nickel steel were used for the test and were irradiated eight hours. Moisture from the breath condensed differently on the exposed and unexposed surfaces, rendering the two easy to distinguish. On the exposed part the drops were larger than on the unexposed part, and the surface looked as if a very thin oil film had been spread over it, making it less easily wetted than the unexposed surface. In the case of medium-carbon steels, very noticeable corrosion of the exposed spots was found to occur after four condensations of moisture, although the rest of the surface was hardly attacked. Chromium and nickel steels did not show any corrosion, although there was the same difference in appearance between the exposed and unexposed surfaces. Jameson[105] has described apparatus for testing the weathering properties of steel plates by exposure to water sprays and ultraviolet rays. Enos[106] believes ultraviolet light increases somewhat the rate of corrosion of various steels. Similar effects are probable with zinc, lead and aluminum.[107] In daylight or artificial light, the rate of corrosion of Electron alloy in sea water decreases with time, although in darkness it remains constant for several days.[108]

Pfeiffer[109] found that the irradiation of 0.5-mm. films of asphalt on clean iron plates leads to the formation of a hard-shrinking skin formed by polymerization and oxidation. Gödrich[110] states that ultraviolet rays render asphalt more insoluble.

Andrews[111] tests road tar by exposing a 1-mm. layer at 150°C. in a given atmosphere to ultraviolet light at 12 inches for twenty hours, with a sheet of Vita glass interposed. After this the penetration of a standard needle, 100 gm. at 5 sec., shall not be less than 50 at the temperature at which the penetration of the original sample was 100.

Neuber and Herberg[112] find that in petroleum asphalts, diffuse sunlight causes a shrinking of the surface layer with the formation of cracks. The oily constituents decrease with the time of exposure. The petroleum resins increase slightly, but the paraffin and ceresin content are hardly changed. The content of hard asphalt increases considerably. The nitrogen content increases considerably, but the sulfur content is unchanged. The carbon content decreases under the short ultraviolet, although it may increase under sunlight.

An accelerated testing cycle involving alternate exposure to a carbon arc and immersion in water has been described by Strieter and Snoke.[113] The wash water is examined for soluble organic products. Acids and ketones are found.

Moisture in the air accelerates the changes in bituminous coatings which occur during exposure to 420 hours of variable sunlight. Bituminous coal-tar pitch was less affected than were blown or high-vacuum Mexican asphalt bitumen. In pure oxygen, the benzene-insoluble material of blown Mexican asphalt bitumen increased six times, although the sulfur content suffered but little change.[114]

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[104] *Ind. Eng. Chem.*, **16**, 698 (1924).

[105] Jameson, C. W., British P. 283,539, Jan. 13, 1927.

[106] Enos, G. M., *Ind. Eng. Chem.*, **17**, 793 (1925); see also Bannister, C. O., and Rigby, R., *J. Iron Steel Inst.*, **133**, 293P (1936); Lavenets, I. V., *J. Applied Chem. (U.S.S.R.)*, **10**, 1556 (1937); *Chem Abs.*, **32**, 2073 (1938).

[107] Bannister, C. O., and Rigby, R., *J. Inst Metals*, **58**, 227 (1936); *Chem. Abs.*, **30**, 3390 (1936).

[108] Fokeev, V. M., *Vestnik Inzhenerov i Tekh.*, 302 (**1933**); *Chem. Abs.*, **32**, 5762 (1938).

[109] Pfeiffer, J. P., *Verfkroniek*, **8**, 43 (1935); *Chem. Abs.*, **29**, 4853 (1935).

[110] Gödrich, P., *Monatsh.*, **36**, 535 (1915); *Chem. Abs.*, **9**, 3127 (1915).

[111] Andrews, R. S., *Gas J.*, **205**, 206, 259 (1934); *Chem Abs.*, **28**, 2162 (1934).

[112] Neuber, F., and Herberg, E., *Mitt. tech. Versuchsamtes*, **24**, 71 (1935); *Chem. Abs.*, **30**, 4658 (1936).

[113] Strieter, O. G., and Snoke, H. R., *J Research Bureau of Standards*, **16**, 481 (1936); *Chem. Abs.*, **30**, 5326 (1936).

Ried and Rusleitner [115] find that the activity of natural or artificial fertilizers can be modified by irradiations.

The use of ultraviolet light to ionize air has been suggested as a means of removing static electricity from air in which sprays cannot be avoided.[116] It is also mentioned by Leboucher [117] for preventing the accumulation of charges in the manufacture of linoleum, celluloid, etc. Rathier [118] states that static electricity can be effectively discharged from rolls of paper 750 mm. long and 600 mm. in diameter by exposing the end of the roll for ten minutes at a meter from a mercury arc. This short exposure does not affect the color of the paper. Allingham [119] proposed to make the ionizing of air by ultraviolet light the basis of a method for partially separating the gases.

Kögel [120] in making sound records, uses gelatin and a light-sensitive organic tanning compound. The records are fixed by exposure to light.

Spectrographic Analysis. The applications of spectroscopy in industrial chemistry are so varied and the methods employing the emission spectra of the substances (elements) sought are so intricate that a discussion is not possible in a limited space. It is proving of increasing importance in metallurgy, mining, and in many other fields. A number of books and review articles are available.[121] Of the 27 elements discovered since 1860, fifteen were discovered as a result of optical spectroscopy, four by x-ray spectroscopy, two by their radioactive properties and six by their chemical properties.[122]

Analytical determinations can be made with great accuracy and a few thousandths of a milligram of metals are determinable. However, the accuracies vary from metal to metal and much experience is required for the effective handling of these methods. Histologists have adapted them to the determination of elements in definite portions of tissue sections, *e.g.*, to the determination of calcium in the various coats of the aorta.

Ultraviolet absorption spectra are being more and more widely employed both in analysis and in the study of the constitution of organic compounds. The similarity of many types of absorption spectra is, however, such that the analytical uses of the method are limited. It has been of particular importance in the development of the knowledge of the constitution of vitamins, hormones, and degradation products of chlorophyll and hemoglobin. Illustrative examples of the utility of the method have been given by Fromherz.[123]

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[114] Walther, H., *Asphalt Teer Strassenbautech.*, **36,** 1001 (1936), *Chem. Abs.*, **31,** 1597 (1937).

[115] Ried, O., and Rusleitner, K., Austrian P. 136,025, Dec. 27, 1933; *Chem Abs.*, **28,** 2456 (1934)

[116] Bachhaus, A. A., *Am Dyestuff Rept.*, **16,** 645, 660 (1927), *Chem. Abs.*, **22,** 127 (1928).

[117] Leboucher, P. J M., French P. 675,109, Oct. 4, 1928; *Chem. Abs*, **24,** 2815 (1930).

[118] Rathier, J., *Papier*, **37,** 83 (1934); *Chem. Abs.*, **28,** 2898 (1934).

[119] Allingham, J, U. S P. 1,553,737, Sept. 15, 1925; *J. Soc. Chem. Ind.*, **44,** 904 (1925).

[120] Kögel, G., U. S. P. 2,068,919, 1937, *Chem. Abs.*, **31,** 1916 (1937).

[121] Gerlach, W., and Schweitzer, E., "Foundations and Methods of Chemical Analysis by Emission Spectra," London, Adam Hilger, Ltd., 123 pp., 1931.

Fitch, A. A.: "Spectrum Analysis in Mineralogy," London, Adam Hilger, Ltd., 52 pp, 1931.

Smith, D. M.: "Bibliography of Literature on Spectrum Analysis," London, British Non-ferrous Metals Research Association, 20 pp.

Crook, W. J.: "Metallurgical Spectrum Analysis," Stanford Univ. Press, 82 pp.

Gerlach, W., and Gerlach, W.: "Clinical and Pathological Applications of Spectrum Analysis, with notes on Spectrography in Chemistry and Mineralogy and Tables for Qualitative Analysis," Leipzig, L. Voss, 1933.

Owens, J. S., *Ind. Eng. Chem. (Anal. Ed.)*, **10,** 64 (1938).

[122] Eddy, C. E, *Chem. Eng. Mining Rev.*, **23,** 309 (1931); *Chem. Abs.*, **25,** 3918 (1931).

Interesting applications have been made of emission spectrography to the study of the flames in an internal combustion engine, particularly when lead tetraethyl and other antiknocking agents are employed.[124]

Fluorescence Analysis. In connection with various topics in the preceding chapters note has been made of the use of fluorescence methods for various analytical determinations. Many other applications of the use of fluorescence in filtered ultraviolet light exist and the method has stimulated a very large number of papers far too great for discussion here. Since no photochemical reactions are necessarily involved, it is unnecessary to devote space to the consideration of the details, particularly since there exist books devoted to the subject.[125] Suffice it to state that the method finds application in the study of documents for age or falsification,[126] It is also used for the detection of fraud in paintings,[127] or of the falsification of water marks in paper,[128] and for other purposes in criminology.[129] It finds varied application in industrial chemistry.[130] For example, the fluorescence of glass may be utilized in control of manufacture and in detection of the age and condition of glass.[131] The so-called "natural" fluorescence has been stated to be dependent upon the physical nature of the glass as well as on its chemical properties. Also, the state of oxidation of the metal or other elements which give fluorescence to the whole was said to be an important factor. In this instance, ultraviolet light may serve as a method of control.

The characteristic fluorescence of glasses has been reported to furnish a method for identification. This was said to be particularly useful in the case of high-priced specialty glasses which sometimes are subject to fraudulent imitation. In some instances there may be introduced into the glass small proportions of substances which would render the glass highly fluorescent in ultraviolet light, without altering the properties and appearance in visible light. It is interesting to note that a fluorescence test may be employed to identify certain of the imitation glasses, such as synthetic resins.[132]

In most of the methods proposed, the ultraviolet light source is used in a dark room in conjunction with a nickel oxide filter which transmits only the region between 3000 and 4000A. Many substances irradiated by these wave-lengths, either powder, dry or in solution, exhibit characteristic fluorescence colors which, in some cases, may serve for the identification of the substances. Although minerals are well known to exhibit brilliant colors, it has been shown that various samples of the same mineral may exhibit different colors, so that the importance of the method is receding. It is, however, of value in some cases in the study of the conditions under which the mineral was originally deposited.

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[123] Fromherz, H., *Chem. Ztg.*, **60**, 445 (1936).

[124] Henne, A. L., and Clark, G. L., *Compt. rend.*, **184**, 26 (1927); Clark, G. L., and Thee, W. C., *Ind. Eng. Chem.*, **18**, 528 (1926); Clark, G. L., and Henne, A. L., *J. Soc. Automotive Eng.*, **20**, 264 (1927); Clark, G. L., *J. Soc. Automotive Eng.*, **23**, 167 (1928); Clark, G. L., and Smith, H. A., *J. Phys. Chem.*, 659 (1927); Rassweiler, G. M., and Withrow, L., *Ind. Eng. Chem.*, **24**, 528 (1932).

[125] Danckwortt, P. W., "Luminescenz Analyse," Leipzig, Akad. Verlags, 1934.
Bernheim, G., and Guyot, M., "Traite d' analyse par les ultraviolets filtrés." Paris, Maloine, 1932.
Radley, J., and Grant, J., "Fluorescence Analysis in Ultraviolet Light." 2nd. ed., London, Chapman & Hall, 1935.
Haitinger, M., "Die Fluorescenzanalyse in der Mikrochemie." Vienna, Emil Haim & Co.
Déribéré, M., "Les applications pratiques de la luminescence. Fluorescence. Phosphorescence. Lumière noire." Paris. Dunod.

[126] Kögel, G., *Sitzungsber. Preuss. Akad. Wiss.*, **37**, 97 (1914); Fonzes-Diacon, Faucon and Reynaud, *Ann. fals.*, **17**, 20 (1924); Mellet and Bischoff, M. A., *Compt. rend.*, **181**, 868 (1925); Bonacini, C., *Brit. J. Photography*, **75**, 36 (1928); *Chem. Abs.*, **22**, 1737 (1928); Mezger., O., *Chem. Ztg.*, **53**, 965, 985, 1006 (1929); Grant, J., *Analyst*, **58**, 603 (1933); Callo, A., British P. 402,136 (1933); Wood, H. P., U. S. P. 2,016,474 (1935); Mitchell, C. A., *Analyst*, **58**, 532 (1933).

[127] Eibner, A., *Angew. Chem.*, **45**, 301 (1932).

[128] Grant, J., *Analyst*, **59**, 749 (1934).

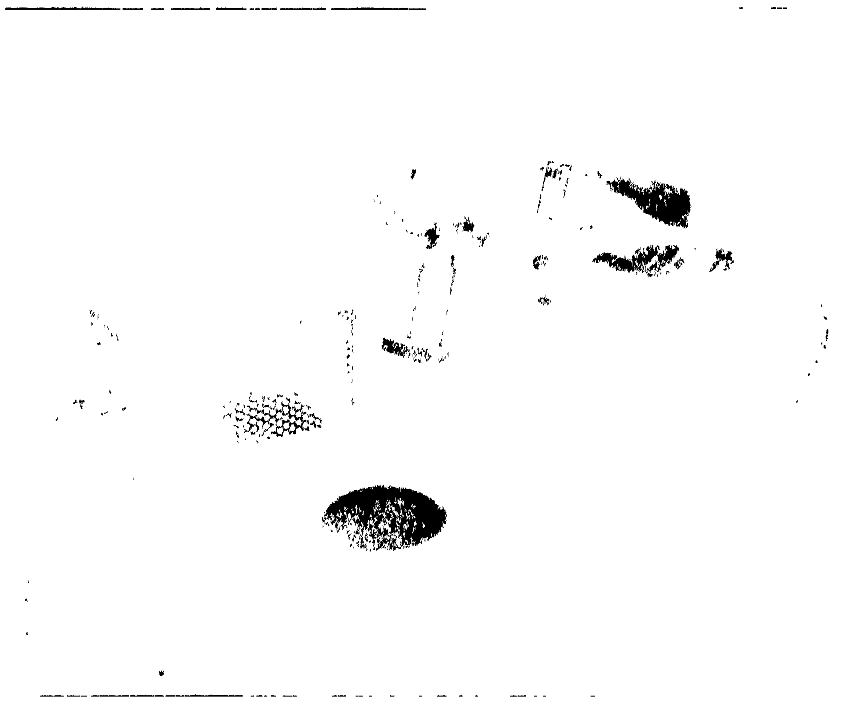
[129] Mitchell, C. A., *Medical-legal Criminol. Rev.*, 3, 3 (1935).

[130] Muir, J., *Ind. Chemist*, **9**, 49 (1933); Grant, J., *Ibid.*, **14**, 277, 289 (1938).

[131] J. Grant, *Ceramic Industry*, 420, June, (1936).

[132] See Carleton Ellis, "The Chemistry of Synthetic Resins," New York, Reinhold Publishing Corp., 1935.

The method is not adapted to the identification of organic compounds by a systematic procedure. It has also been shown that many compounds which, like quinine, fluoresce brilliantly, owe this property to the presence of traces of as yet unidentified impurities. Nevertheless, there are many instances in which the method offers considerable aid in the rapid control of technical processes.



Courtesy National Carbon Co., Inc.

FIGURE 131. Eveready Fluoray Apparatus.

In Germany, there was introduced the Hanau "Quarzlampen für Analyse" as a source for this purpose. An apparatus which employs visible light, sunlight or daylight is the Callophane, merely a light-tight box for the specimen, which is illuminated by a filter of special glass on one side of the box and having provision for viewing the specimen under a black cloth thrown over the head of the observer. Figure 131 shows the Eveready carbon arc apparatus (Fluoray) devised for the purpose by the National Carbon Co. A 4-mm. Corning red-purple ultrafilter No. 587 transmits chiefly the 3650A line.

The method is extremely rapid, sensitive and does not alter the object investigated. The personal equation of the observer enters into the color readings to a considerable extent, but recently efforts have been made to adapt the method to a quantitative recording of the intensities of the fluorescence at various wave-lengths. It is interesting to note that in a rather neglected paper, Desha[133] proposed a method of quantitative analysis by comparative fluorescence (fluoremetry).

Since the fluorescence of certain compounds changes with the pH of the solution in which they are dissolved, they can be employed as fluorescent indicators in titrations conducted in the light of a Wood lamp.[134]

The fluorescence methods also may be adapted to microscopic objects. A fluorescence microscope was described by Haitinger and Reich.[135, 136]

It has been proposed by Andant[137] to utilize their Raman spectra in the identification of the hydrocarbons present in gasolines.

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[133] Desha, L. J., *J. Am. Chem. Soc.*, **42,** 1350 (1920); see also F. Bandow, *Biochem. Z.*, **295,** 154 (1938).

[134] Dériběré, M., *Documentation sci.*, **6,** 114 (1937); *Chem. Abs.*, **31,** 6086 (1937); *Tiba,* **15,** 349 (1937); *Chem. Abs.*, **32,** 1602 (1938).

[135] Haitinger, M., and Reich, V., *Chem. Fabrik,* 529, 1929; Haitinger, M., "Fluorescenzmikroskopie. Ihre Anwendung in der Histologie und Chemie." Leipzig. Akad. Verlag

[136] For a detailed discussion of modern theories of fluorescence and phosphorescence, see Pringsheim, P.; "Fluorescenz und Phosphorescenz im Lichte der neueren Atomtheorie," Berlin, J. Springer, 1929.

[137] Andant, A., *Chimie et industrie, Special No. 480,* June, 1933; *Chem. Abs*., **27,** 5952 (1933).

Part IV

Biological Applications

Chapter 34

The Photochemical Behavior of Compounds of Biological Significance

An understanding of the processes underlying the biological applications of ultraviolet light demands a knowledge of the photochemical behavior of the compounds present in biological systems. Of the three chief classes of biochemical compounds—proteins, carbohydrates and lipids—the carbohydrates are discussed in Chapter 23. The fats are discussed in Chapter 29. Other lipid reactions have been relatively little studied aside from the well-known conversion of the sterols into the D vitamins. Consideration of this process is deferred to Chapter 39.

LIPIDS

Lecithin solutions, aqueous or alcoholic, absorb radiations in the region of 2970A. Kollath[1] suggested that when skin is irradiated, its lecithin may be the source of some physiologically active substances of which acrolein may be typical. He based this upon the observation that either a very dilute aqueous solution of acrolein or an irradiated aqueous emulsion of lecithin when added to ferrous salts enabled them to aid the growth of the influenza bacillus. Kögel believes irradiation of lecithin or choline by sunlight or ultraviolet light to lessen their power of reducing a silver-metol acetic acid reagent.[2] In the case of lecithin, the acidity increases, because of the liberation of phosphoric and fatty acids, along with glycerol and choline.[3]

Although Becking and Gregersen[4] believed the permeability of membranes made from equal proportions of collodion and lecithins to be transitorily increased by illumination, Brooks[5] considered that this is in need of further experimental support.

The ability of cephalin to protect cholesterol sols from the coagulating action of salts is destroyed by intensive ultraviolet irradiation.[6] An irradiated 0.25 per cent cephalin sol does not flocculate gold sols, differing in this respect from irradiated proteins. Neither does it cause the hemolysis of red blood cells, an effect which has been observed in the case of irradiated lecithin sols by Fabre and Simonnet.[7]

Bile acids no longer give the Nakagawa red reaction after ultraviolet irradiation.[8] Such treatment also reduces the ability of sodium glycocholate to detoxify certain organ poisons (lung or intestine).[9]

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[1] Kollath, W., *Klin. Wochschr.*, **6**, 13 (1927); *Chem. Abs.*, **21**, 2009 (1927); see also Spiegel-Adolf, M., *Biochem. J.*, **29**, 2413 (1935).

[2] Kögel, G., *Z. Krebsforsch.*, **46**, 105 (1937); *Chem. Abs.*, **31**, 8670 (1937).

[3] Roffo, A., and Correa, L., *Bol. inst. med. exptl. No 42* (1936); *Rev. sudamericana endocrinol. immunol. quimiotherap.*, **20**, 548; *Chem. Abs.*, **32**, 201 (1938).

[4] Becking, B. L., and Gregersen, M., *Proc. Soc. Exptl. Biol. Med.*, **22**, 130 (1924); *Chem. Abs.*, **19**, 3273 (1925).

[5] Brooks, S. C., *Science*, **61**, 214 (1925). See also Brauner, L., and Brauner, M., *Protoplasma*, **28**, 230 (1937).

[6] Spiegel-Adolf, M., *J. Am. Chem. Soc.*, **57**, 1431 (1935).

[7] Fabre, R., and Simonnet, H., *Bull. soc. chim. biol.*, **10**, 1036 (1928); *Chem. Abs.*, **24**, 1126 (1930)

On irradiation, methyl cholate in chloroform becomes yellow, shows a decreased rotation, and yields on fractional crystallization, a β-ester of lower rotation and higher melting point. A stereoisomeric change is believed to occur at the secondary hydroxyl group of ring III of the ester. Neither the free acid nor its sodium salt in water suffered the isomerization. The β-ester differed from the original α-form in its greatly retarded Mylius reaction, its greater solubility, and its failure to be precipitated by digitonin. A further product of the irradiation was a resin which on saponification yielded a yellow acid, $[\alpha]_D^{20}=25$, with a titration equivalent of 591.7, and probably a condensation product of cholic acid.[10, 11]

Proteins and Amino-acids

The photochemistry of the proteins is best approached by considering first the behavior of their degradation products, the amino- acids. The absorption of ultraviolet light by proteins is very largely due to their ring-containing amino- acids, tryptophane, phenylalanine and tyrosine.[12] These amino- acids exhibit selective absorption between about 2400 and 2900A, the maximum being at about 2750A, at least in the case of tryptophane.[13] In connection with other investigations, Svedberg and co-workers have given ultraviolet absorption curves for a number of proteins, from which it can be readily shown that the selective absorption with maximum at 2750 to 2800A depends in large part upon the content in the proteins of the amino- acids tryptophane and tyrosine. The influence of most of the remaining amino- acids is evident chiefly in the absorption at wave-lengths of 2300A or less. Of recent years many papers,[14] on details of the absorption spectra of proteins have appeared.[15]

Amino- Acids. Tryptophane and tyrosine are sensitive to irradiation with ultraviolet light, absorbing oxygen under its influence.This accounts for most of the oxygen uptake by irradiated plasma, according to Harris.[16]

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[8] Mikami, H., *J. Biochem. Japan*, **14**, 489 (1932); *Chem. Abs.*, **26**, 1968 (1932).

[9] Ito, R., *Folia Pharmacol. Japan.*, **12**, No. 2, 131 (1931); *Chem. Abs.*, **25**, 5507 (1931).

[10] Uraki, Z., *Z. physiol. Chem.*, **207**, 16 (1932); *Chem. Abs.*, **26**, 3802 (1932).

[11] Phosphatides and other lipids are irradiated in a patent of "Pharmagans" Farm. Ins. L. W. Gans, A. G., Kollath, W., and Magistris, H., British P. 311,436, Jan. 10, 1928; *Chem. Abs*, **24**, 920 (1930).

[12] Harris, F. I., and Hoyt, H. S., *Pathology*, **2**, 245 (1919); *Chem. Abs.*, **13**, 2384 (1919).

[13] Holiday, E. R., *Biochem J.*, **30**, 1795 (1936); Feraud, K., Dunn, M. S., and Kaplan, J., *J. Biol. Chem.*, **112**, 323 (1935); **114**, 665 (1936); Heidt, L. J., *J. Biol. Chem.*, **115**, 223 (1936). These references give extensive citations to earlier work.

[14] Shibata, Y., and Asahina, T., *Bull. Chem. Soc. Japan*, **1**, 71 (1926); **2**, 324 (1927); Grinbaum, R., and Marchlewski, L., *Bull. intern. acad. polon. sci., Classe sci. math. nat.*, **A**, 156 (1937); *Chem. Abs.*, **32**, 1576 (1938).

[15] Some of the more important are the following: Abderhalden, E., and Haas, R., *Z. physiol. Chem.*, **155**, 195 (1926); Gioh, G., and Weltner, M., *Ibid.*, **198**, 267 (1931); Vles, F., and Prager, M., *Arch. Phys. Biol.*, **10**, 5 (1932); *Chem. Abs.*, **27**, 5643 (1933); Roche, J., and Dubouloz, P., *Compt. rend.*, **196**, 646 (1933); Marchlewski, L., and Wierzuchowska, J., *Bull. Acad. Polonaise*, **A**, 471 (1928); *Brit. Chem. Abs.*, **A**, 459 (1929); Theorell, H., *Biochem. Z.*, **268**, 55 (1934); Giza, T., *Bull. Intern. Acad Polonaise*, **A**, 421 (1934); *Chem. Abs.*, **29**, 2977 (1935); Porcher, C., Volkringer, H., and Brigando, J., *Lait*, **14**, 1041 (1934); *Chem. Abs.*, **29**, 3697 (1935); Hicks, C. S., and Holden, H. F., *Australian J. Exp. Biol. Med. Sci.*, **12**, 91 (1934); *Chem Abs*, **29**, 2556 (1935); Coulter, C. B., Kabat, E. A., and Stone, F. M., *J. Bacteriol.*, **29**, 54 (1935); *J. Gen. Physiol.*, **19**, 739 (1936); Grinstein, M., *Rev. inst. bacteriol. dept. nacl. hig. (Buenos Aires)*, **7**, 351 (1936); Mitra, B. N., *Indian J. Med. Research*, **24**, 5 (1936); Almquist, H. J., Givens, J. W., and Klose, A., *Ind. Eng. Chem.*, **26**, 847 (1934); Gioh, J., and Faltin, E., *Z. physiol. Chem*, **199**, 13 (1931); Gioh, J., and Weltner, M., *Biochem. Z.*, **273**, 389 (1934); Freudenberg, K., Discherl, W., and Eyer, H., *Z. physiol. Chem.*, **187**, 89 (1930); Vles, F., and Cohn, C., *Arch. Phys. Biol*, **5**, 48 (1926); *Chem. Abs.*, **21**, 2997 (1927); DeBoer, J. H., Dippel, C. J., and Custers, J. F. H., *Rec. trav. chim.*, **52**, 195 (1933); Smith, F. C., *Proc. Roy. Soc.*, **104B**, 198 (1929); Asahina, T., *Bull. Chem. Soc. Japan*, **4**, 202 (1929); **5**, 354 (1930). For a collection of over two hundred curves for the absorption of proteins, carbohydrates and fats, see Ellinger, F., *Tabulae Biologicae*, **12**, 291 (1937).

[16] Harris, D. T., *Biochem. J.*, **20**, 288 (1926).

Berthelot and Amoreux find tryptophane forms indole-3-acetic acid, detectable after ten minutes of mercury arc irradiation of a solution of 0.5 gm. per liter in a quartz flask. The change is retarded by acidification to pH 4.5.[17]

The non-aromatic amino- acids, such as glycine, alanine, valine, leucine, and aspartic acid, either do not show an increased rate of oxidation when irradiated, or show it less readily. Lieben[18] found that sensitizers such as hematoporphyrin increase the oxygen absorption of the aromatic amino- acids in the light of the quartz lamp and even enable them to show some activity in diffused daylight. The velocity of the oxidation is increased by alkalinity and, in the case of tryptophane, by the addition of formaldehyde. When combined in proteins, the destruction of these amino- acids by light is retarded. They are of particular interest because of their possible participation in the mechanism by which the pigment melanin, or a related substance, may be formed during tanning by sunlight.

Arnow[19] finds irradiation to convert *l*-tyrosine into *dopa*(*l*-3,4-dihydroxyphenylalanine), which itself can be destroyed by prolonged irradiation. An oxidase of certain skin cells (the melanoblasts) converts *dopa* into the tan pigment melanin.

The absorption spectra of the aliphatic amino- acids have been interpreted as indicative of a zwitterion structure $^{+}NH_3CH_2COO^{-}$.[20]

The wave-length at which the continuous absorption of the glycine cation, $NH_3^{+}CH_2COOH$ begins has been considered by Onslow, Foster and Klingler[21] to afford a measure of the energy required for its dissociation into a hydrogen ion and the zwitterion $NH_3^{+}\cdot CH_2\cdot COO^{-}$. In water, it begins at the wave-number 51894 and in hydrochloric acid at 51813, corresponding to 146.86 and 146.63 kcal., respectively. The dissociation frequency is regarded as the sum of the limiting frequency of the Balmer series for hydrogen and of a natural vibration frequency of the molecule-ion, the latter term varying in different amino- acids inversely as the square root of the molecular weight of the zwitterion. In alkaline solution, the glycine cation exists as $NH_3^{+}CH_2COONa$. Dissociation occurs at a wave-number corresponding to 138.59 kcal. Irradiation with ultraviolet light causes polymerization.

After irradiation by a mercury arc for fifteen hours, a $0.1N$ aqueous glycine solution increased in conductivity from 1.54×10^{-5} to 71.20×10^{-5}. Its pH increased from 4.8 to 7.45. These changes are due to the formation of ammonia as a result of hydrolysis;

$$NH_2CH_2COOH + H_2O \longrightarrow OHCH_2COOH + NH_3$$

Glycolic acid, but no acetic acid, was formed and the occurrence of side reactions was indicated by the evolution of a gas rich in carbon monoxide. The reaction was most rapid, according to Henri, Weismann and Hirschberg,[22] at pH 3, declining with increasing pH to a minimum at pH 6 and then increasing slowly. Although the absorption begins at about 2400A, wave-lengths less than 2205A are required to produce the decomposition. The quantum yields are about 0.09 for glycine, 0.1 for alanine, and 0.06 for the compound betaine. The rate of reaction is much greater in alanyl-glycine than in glycine and in phenylalanine than in alanine.[23]

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[17] Berthelot, A., and Amoreux, G., *Compt. rend.*, **206**, 699 (1938).

[18] Lieben, F., *Biochem. Z.*, **184**, 453 (1927).

[19] Arnow, L. E., *J. Biol. Chem.*, **120**, 151 (1937); *J. Phys. Chem.*, **42**, 415 (1938).

[20] Ley, H., and Zschacke, F. H., *Ber.*, **57B**, 1700 (1924); Leuthardt, F., and Pfister, M., *Helv. Chim. Acta*, **16**, 228 (1933); Ueda, H., *J. Chem. Soc. Japan*, **50**, 502 (1929); *Chem. Abs.*, **26**, 91 (1932); Ley, H., and Arends, B., *Ber.*, **61B**, 212 (1928).

[21] Onslow, G. A., Foster, M. L., and Klingler, C., *J. Biol. Chem.*, **103**, 81 (1933).

[22] Henri, V., Weizmann, C., and Hirschberg, Y., *Compt. rend.*, **198**, 168 (1934); **199**, 1205 (1935).

[23] Weizmann, C., Hirschberg, Y., and Bergmann, E., *J. Am. Chem. Soc.*, **60**, 1799 (1938).

Aspartic acid also is hydrolyzed by ultraviolet light.[24] Irradiation of *l*-aspartic acid produces a new absorption band at 2650A, according to Becker,[25] which is not observed in the case of either asparagine or malic or tartaric acids. Becker showed later that both *l*-aspartic acid and *l*-asparagine yield acetaldehyde upon irradiation. The decomposition products of glycylglycine are different. Because of their α-hydroxyl groups, *dl*-serine and *dl*-lactic acid react differently from *dl*-alanine.[26]

The splitting of ammonia from amino- acids as a result of irradiation has also been studied by Lieben and Urban;[27] only the α-amino- group undergoes this reaction. It is greatest in histidine, 88 per cent, and next in cystine, 32.7 per cent. It is twice as great in lysine, 20.9 per cent, as in arginine, 9.4 per cent. The total decomposition of histidine, tyrosine, or tryptophane, as measured colorimetrically, did not agree with the amount of ammonia evolved, indicating the occurrence of secondary reactions, as had been suggested by Weizmann in the case of glycine. Guanidine was resistant and did not evolve ammonia when irradiated. The amino- group in guanine or in anthranilic acid or benzidine is displaced as easily as when it is present in a side chain.

Hippuric acid is very stable in sunlight.[28] The irradiation of hydroxyproline solutions by a quartz lamp produces two new absorption bands at 2570 and 3130A; the latter does not appear if the solid is irradiated.[29]

Ellinger [30] found that irradiation of a 1-per cent solution of histidine hydrochloride by a quartz mercury arc yields traces of a decomposition product detected pharmacologically by its histamine-like action. Histamine is the product of the decarboxylation of histidine. Photocatalysts did not accelerate the rate of the conversion, which, within certain limits, was unaffected by the pH of the solution or by the duration of the irradiation. Further application of radiations of the wave-lengths 2970 and 3020A caused a loss of the pharmacological activity of the irradiated solutions. During the irradiation of histidine, changes in the absorption spectra, interpreted as indicative of the decarboxylation of histidine,[31] were observed. Becker,[32] however, pointed out that the similarity of the absorption spectra of histidine and of histamine is such that the optical method is unsuited for following the decarboxylation of histidine. Ellinger [33] later admitted that what he had regarded as the characteristic absorption of histidine hydrochloride in the longer wave-length region of the ultraviolet had been due to the presence of traces of iron compounds as impurities.

Nevertheless, renewed interest in the reaction was aroused by the demonstration by Holtz [34] that histamine is produced by the irradiation of a 1 : 150 solution of histidine at pH 12 in the absence of oxygen. He was able to isolate 7 mg. of histamine, identified by melting point and analysis of the crystalline pictrate, chloroaurate and chloroplatinate, from the products of irradiation of 1 gm. of histidine.

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[24] Weizmann, C., Bergmann, E., and Hirschberg, Y., *Ibid*, **58**, 1675 (1936).

[25] Becker, J. P, *Strahlentherapie*, **50**, 357 (1934), *Chem Abs.*, **28**, 5338 (1934).

[26] Becker, J. P., *Strahlentherapie*, **52**, 531-537 (1935); *Brit. Chem. Abs.*, **A**, 437 (1936).

[27] Lieben, F., and Urban, F. F., *Biochem. Z.* **239**, 250 (1931), *Oesterr Chem. Ztg.*, **37**, 20 (1934)

[28] Enselme, J., and Pozzi, M., *Bull. soc. chim. biol.*, **17**, 283 (1935).

[29] Becker, J. P, *Strahlentherapie*, **48**, 296 (1933); *Chem. Abs*, **28**, 1064 (1934)

[30] Ellinger, F., *Archiv exp. Path. Pharmakol*, **136**, 129 (1928)

[31] Ellinger, F., *Biochem. Z.*, **215**, 279 (1929).

[32] Becker, J. P., *Arch. ges. Physiol (Pflügers)*, **228**, 751 (1931).

[33] Ellinger, F., *Biochem. Z.*, **248**, 437 (1932).

[34] Holtz, P., *Klin. Wochschr.*, **12**, 1613 (1933); *Archiv exp. Path. Pharmakol.*, **175**, 97 (1934).

Ellinger[35] had not been able to identify the irradiation products chemically or spectroscopically after the irradiation of histidine, dry or in solution, but observed that the irradiated solution excites the intestine of a guinea pig. The extracts made with hot chloroform also lowered the blood pressure. Since the injection of histamine into the skin is known to lead to the production of an erythema, Ellinger suggested that the erythema of sunburn may be due to the production of a histamine-like substance from histidine in the upper layers of the epidermis. It was possible to obtain considerable amounts of such substances from even the non-irradiated skin of guinea pigs, although such extracts were never more active than those of irradiated samples.

Szendrö[36] maintains that imidazoleacetaldehyde is the material formed in the irradiation of histidine. On the other hand, according to Wrede and Holtz,[37] the irradiation of imidazolylethyl alcohol does not yield depressor substances.

The oxidation of cystine is not induced by irradiation, according to Harris,[38] and cysteine takes up oxygen so rapidly in darkness that any acceleration produced by ultraviolet light is negligible in comparison with that produced in the case of tryptophane or tyrosine.

The energy required for the dissociation of cystine in hydrochloric acid solutions is, from the absorption spectrum, 70.8 kcal.[39] Lieben and Molnar,[40] find that, although both cystine and cysteine do decompose under the quartz mercury arc, the process proceeds much more slowly than in the case of the aromatic amino-acids. In diffused daylight, the destruction of cystine occurs only in an alkaline medium. Since cysteine oxidizes spontaneously in an alkaline solution, its behavior must be studied in an acid medium and for this a photosensitizer, such as hematoporphyrin, is required in daylight. In the arc light, however, there is a slow decomposition in the absence of a sensitizer. Szendrö, Lambert and Wrede[41] claim that *l*-cysteine is formed in 5-per cent yields when cystine is irradiated with ultraviolet light.

Rao and Dhar[42] studied the photo-oxidation of amino- acids in sunlight in the presence of such sensitizers as titanium dioxide, zinc oxide and alumina. The products formed from the aliphatic representatives included aldehydes, carbon dioxide and ammonia. Monoaminodicarboxylic acids acted less readily than the monoaminomonocarboxylic acids. Anthranilic acid gave aniline and carbon dioxide. Ort has given some attention to the catalytic influence which amino- acids may exert upon the oxidation of sugars irradiated in the presence of hydrogen peroxide[43]

It is apparent from a consideration of the observations recorded in these paragraphs that, although a quartz mercury arc produces certain changes in amino-acids, the radiations available in sunlight or even from artificial sources under the usual conditions of their therapeutic applications, are incapable of affecting the amino-acids other than those which contain an aromatic, indole or imidazole ring.

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[35] Ellinger, F., *Archiv exp. Path. Pharmakol.*, **153**, 120 (1930); *Strahlentherapie*, **38**, 521 (1930); *Chem Abs.*, **25**, 526 (1931).

[36] Szendrö, P., *Arch. ges. Physiol. (Pflüger's)*, **228**, 743 (1931); *Chem. Abs.*, **26**, 1862 (1932).

[37] Wrede, F., and Holtz, P, *Arch. ges. Physiol (Pflüger's)*, **234**, 432 (1934); *Chem. Abs.*, **28**, 5477 (1936).

[38] Harris, D. T., *Biochem. J.*, **20**, 288 (1926)

[39] Foster, M. L., Anslow, G. A., and Barnés, D., *J. Biol. Chem.* **89**, 665 (1930); **Barnés, D.**, *Anales Soc. Espan. Fis. Quim.*, **28**, 1386 (1930); *Chem. Abs.*, **25**, 2366 (1931).

[40] Lieben, F., and Molnar, E., *Biochem. Z.*, **230**, 347 (1931).

[41] Szendrö, P., Lambert, V., and Wrede, F, *Z. physiol. Chem.*, **222**, 16 (1933).

[42] Rao, G. G., and Dhar, N. R., *J. Indian Chem. Soc.*, **11**, 617 (1934); *Chem. Abs*, **29**, 1326 (1935).

[43] Ort, J. M., *J. Phys. Chem.*, **33**, 825 (1929).

In general, there is, on the irradiation of amino- acids with light of sufficiently short wave-length, an evolution of ammonia and a shift of the absorption spectrum to somewhat longer wave-lengths.[44]

The optical rotations of optically active dipeptides are unaltered by exposure to ultraviolet light, but solutions of the corresponding 2,5-diketopiperazines show a diminution in rotation which soon reaches a constant value. Traces of ammonia and carbon dioxide can be detected after irradiation in air, but not in nitrogen, so that the mechanism probably involves oxidation. Solutions of silk peptones show similarly altered rotations.[45]

The irradiation of a solution of Witte's peptone produces a skin on the surface. This skin fails to give the biuret reaction. The tyrosine content is reduced, as is that of histidine and there is no tryptophane present. Since the amino-nitrogen content in this skin is found to be reduced, it is probable that the production of plasteins may have occurred. The minimum amount of skin is formed at pH 5.5. On removal of the film, a new one forms on further irradiation. Solutions of the peptones from casein or silk fail to behave in a similar manner.[46]

Behavior of Proteins on Irradiation.[47] In 1913, Bovie[48] reported that fresh egg albumin, on exposure in a quartz tube at 10 cm. from a mercury arc lamp at room temperature, began to show a feathery coagulum on the walls nearest the lamp and after 35 hours had become fully coagulated and possessed a peculiar, strong odor. When an aqueous solution was employed, less time was required for the coagulation. The product formed settled to the bottom of the tube. Crystalline albumin not freed from ammonium sulfate coagulated more rapidly than fresh egg-white. After dialyzing away the salt, the protein was still more sensitive and showed some coagulation even when exposed in glass tubes. Ox-serum was also coagulated in quartz tubes. No coagulation occurred at zero, but if the solution was then warmed a few degrees it became turbid. If the temperature was then quickly reduced, the solution again became clear. It was suggested that light alters the protein at low temperatures, but that only at higher temperatures does there occur a second change leading to the production of a visible coagulum.[49]

Many observations have since been made of the phenomenon. In the case of serum albumin, Teichler,[50] believed the coagulating action, although not the primary photochemical process, to be dependent upon the relative amounts of sodium and calcium ions present.

The question has been frequently raised as to whether the mechanism is the same as that of the coagulation by heat. Bovie believed this to be the case, since he found the coagulated material soluble in dilute alkali, but insoluble in alcohol, water or dilute acid. Spiegel-Adolf and Krumpel.[51] found that the absorption spectrum changes during heat coagulation in a manner similar to that during irradiation, but that the changes were quantitatively less in the former case. However, Spiegel-Adolf found also, at least in the case of serum albumin,[52] that the coagulum formed by irradiation differed from that formed by heat in not being rendered water-soluble by dilute alkali followed by dialysis. After irradiation in the presence of hydrochloric acid, serum albumin can be salted out, but this differs from the behavior on heating in the presence of acid. In spite of these differences, serum albumin heated or irradiated in the presence of sodium hydroxide shows the same behavior to neutral salts. The presence of larger concentrations of neutral salts does not prevent the coagulation of serum albumin during irradiation, but the presence of multivalent ions does inhibit the precipitation. Potassium thiocyanate does not inhibit the irradiation coagulation and cannot bring the product into solution, differing in this respect from its effects on heat coagulaton.

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[44] Allen, A. J., Steiger, R. E., Magill, M. A., and Franklin, R. G., *Biochem. J.*, **31**, 195 (1937); Magill, M. A., Steiger, R. E., and Allen, A. J., *Biochem. J.*, **31**, 188 (1937).

[45] Abderhalden, E., and Haas, R., *Z. physiol. Chem.*, **155**, 195, 200 (1926); **166**, 78 (1927); **160**, 256 (1926); **164**, 1 (1927); Hünecke, H., *Ber.*, **60B**, 1451 (1927); Ley, H., and Arends, B., *Ber.*, **61B**, 212 (1928); Abderhalden, E., and Rossner, E., *Z. physiol. Chem.*, **176**, 249 (1928); **178**, 156 (1928); Asahina, T., *Bull. Chem. Soc. Japan*, **4**, 202 (1929); Guthmann, H., Schwerin, K., and Stähler, F., *Strahlentherapie*, **39**, 401 (1931); *Chem. Abs.*, **25**, 2448 (1931).

[46] Lieben, F., and Jesserer, H., *Biochem. Z.*, **275**, 367 (1935).

[47] This subject has been reviewed in considerable detail by Arnow, L. E., *Physiol. Revs.*, **16**, 671 (1936).

[48] Bovie, W. T., *Science*, **24**, 374 (1913).

[49] Bovie, W. T., and Hughes, D. M., *J. Gen. Physiol.*, **1**, 323 (1919); Bovie, W. T., and Klein, A., *Ibid.*, **1**, 331 (1919); Bovie and Daland, G. A., *Am. J. Physiol.*, **66**, 55 (1923).

[50] Teichler, G., *Arch. ges. Physiol (Pflüger's)*, **227**, 558 (1931); *Chem. Abs.*, **25**, 4289 (1937).

[51] Spiegel-Adolf, M., and Krumpel, O., *Biochem. Z.*, **208**, 45 (1929).

Clark[53] pointed out that only at pH values near the isoelectric point is albumin coagulated by either light or heat. At other pH values, it remains clear on irradiation but has been altered by the process so that it behaves toward electrolytes as a globulin. Other workers, notably Abderhalden, observed that a slight decrease in pH occurs during the irradiation of globulin and, in the presence of sodium chloride, albumin solutions. The optical rotation also decreases, but the conductivity increases slightly. The increase in acidity was also observed by Mond,[54] who found the viscosity increased, and the surface tension decreased. The latter effect was less in the case of albumin than of globulin.[55]

Stedman and Mendel[56] extended the investigations to about twelve purified proteins. In general, there was a lowering of the coagulation temperature, together with the production of an odor and a yellow tint, and in some cases, an increase in the specific rotation. These changes were independent of the presence of water, electrolytes and oxygen. In tests of some fourteen proteins, it was found by Spiegel-Adolf and Pollaczek[57] that bacterial contamination of the solutions retarded their coagulation during irradiation. The retarding effect persisted even after the infection had spontaneously died.

Rajewsky[58] found the primary denaturation process independent of temperature, only the conglomeration of the denatured particles being accelerated by a rise in temperature. Gentner and Schwerin[59] followed the coagulation by following the changes in the number of particles exhibiting Brownian movement. At the isoelectric point of egg albumin, three processes rather than two may be recognized as involved in the mechanism of coagulation, according to Clark.[60] Following the primary photo-denaturation, she believes there ensues a reaction between the denatured molecule and water, following which there is a flocculation of the denatured molecules to form the coagulum. The first denaturation is a monomolecular process, which, in agreement with Rajewsky, is independent of temperature. The reaction with water has, however, a high temperature coefficient—over ten. The reaction occurs rapidly at 40°C., a temperature at which heat denatura-

[52] Spiegel-Adolf, M., *Biochem. Z.*, **186**, 181 (1927).

[53] Clark, J., *Am. J. Physiol.*, **73**, 649 (1925).

[54] Mond, R., *Arch. ges. Physiol. (Pflüger's)*, **196**, 540 (1922); **200**, 374 (1923); *J. Chem. Soc.*, **123**, and **124**, (I), 868.

[55] Other early observations of this type were due to Schanz, F., *Archiv ges. Physiol. (Pflüger's)*, **164**, 445 (1916); *Chem. Zentr.* **87**, II, 670 (1916); *Chem. Abs.*, **10**, 1656 (1916), and to Kreibich, C., *Arch. Path. Anat.*, **222**, 28 (1916); *Chem. Abs.*, **14**, 2023 (1920).

[56] Stedman, H. L., and Mendel, L. B., *Am. J. Physiol.*, **77**, 199 (1926).

[57] Spiegel-Adolf, M., and Pollaczek, K. F., *Biochem. Z.*, **214**, 175 (1929).

[58] Rajewsky, B., *Biochem. Z.*, **227**, 372 (1930); *Klin. Wochschr.*, **10**, 1673 (1931).

[59] Gentner, W., and Schwerin, K., *Biochem. Z.*, **227**, 286 (1930).

[60] Clark, J., *J. Gen. Physiol.*, **19**, 199 (1935).

tion is inappreciable. Mirsky and Pauling[61] suggest that the primary absorption process causes a break in the native protein molecule which enables it to suffer denaturation at a temperature lower than that otherwise required.

Little is known as yet of the precise nature of this primary process. Lampert and Wels[62] noted during irradiation in the absence of oxygen the formation of a substance with sulfhydril reactions which cannot, however, be separated from the proteins by ultrafiltration or by precipitating the protein with colloidal ferric hydroxide. Mirsky and Anson[63] observed that the number of sulfhydril groups in egg albumin coagulated by ultraviolet light is equivalent to that in samples coagulated by typical denaturing agents.

Other observations of chemical decompositions involved have been occasionally made. Hoffmeister[64] claims that after five hours of irradiation of serum albumin and peptone, the values for acetaldehyde were as high as 68 and 108 mg., respectively, as compared with 18 and 8 mg. in non-irradiated controls. Howitt[65] also suggested that formaldehyde or some similar substance is produced from egg albumin, and that this, by reacting with amino- groups, might account for an observed increased acidity. An alkaline reaction favors the last step and tends to lessen the possibility of a reducing action by the aldehyde.

Gelatin and globin (and also the alkaloid caffeine), when irradiated in weakly acid solutions, yield ammonia, according to Eckstein and Lieben.[66] These observers do not believe an increase in amino- nitrogen to be due to a cleavage of peptide linkages, since peptides are not hydrolyzed under these conditions. They also exclude arginine as the source and believe that both the ammonia and the increased amino-nitrogen originate from the heterocyclic rings of histidine, proline and hydroxylproline. Lieben and Jesserer,[67] however, admit that the peptide linkages in proteins may be less resistant than they are in peptones and peptides, so that it may not be necessary to conclude that the origin is exclusively the breaking of heterocyclic rings.

Much attention has been devoted to the changes wrought by irradiation in the collodial behavior of the proteins. Mond[68] believed that the stability of solutions of serum globulin and fibrinogen are increased since their coagulation temperatures were raised.

According to Cossu,[69] non-irradiated samples of serum albumin show a minimum in the surface tension-pH curve at the isoelectric point, but after irradiation there is a maximum at the isoelectric point and another at a point on the acid side. The protein is no longer stable at the isoelectric point as shown by the fact that the solutions are slightly turbid.

Monomolecular albumin films on irradiation dissolve completely in about two hours.[70] Mitchell[71] found that the phase-boundary potentials of egg albumin films increase when irradiated by the 2537A line. The solid film liquefies. It was suggested that certain CO—NH linkages in the main polypeptide film may be hydrolyzed. It could be shown that this linkage is broken in stearic anilide to the extent of at least 95 per cent, the quantum yield being unity, but varying with the molecular orientation in a manner for which a theory was given. Mitchell called attention to the interesting possibilities offered in biological work by the fact that the photochemistry of monomolecular layers offers a means of studying the effects of orientational factors.

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[61] Mirsky, A. E., and Pauling, L., *Proc. Nat. Acad. Sci*, **22**, 439 (1936).

[62] Lampert, U., and Wels, P., *Archiv exp. Path. Pharmakol*, **175**, 554 (1934).

[63] Mirsky, A. E., and Anson, M. L., *J Gen. Physiol*, **19**, 427 (1936). See also Wenig, K., and Jirovec, O., *Biochem. Z.*, **295**, 405 (1938).

[64] Hoffmeister, A., *Z. physiol. Chem*, **205**, 183 (1932).

[65] Howitt, F. O., *Nature*, **125**, 412 (1930).

[66] Eckstein, H. C., and Lieben, F., *Biochem. Z*, **263**, 366 (1933).

[67] Lieben, F., and Jesserer, H., *Biochem. Z.*, **275**, 367 (1935).

[68] Mond, R., *Archiv ges. Physiol. (Pflüger's)*, **196**, 540 (1922); **200**, 374 (1923); *J Chem Soc.*, **123-4**, 868 (1923).

[69] Cossu, F., *Bull. soc. ital. biol. sper.*, **10**, 973 (1935), *Chem. Abs.*, **30**, 2589 (1936).

[70] Rideal, E. K., *Kolloid-Z.*, **61**, 218 (1932).

[71] Mitchell, J. S., *Proc. Roy. Soc.*, **A155**, 696 (1936).

Among the most carefully conducted and detailed studies of the changes occurring in proteins are those of Spiegel-Adolf.[72] With Krumpel,[73] she showed irradiation to increase the ultraviolet absorption of solutions of electrolyte-free serum albumin in the region 4000 to 2675A, without affecting the location of the absorption maxima and minima. Oxygen was not necessarily present in order to produce these changes. Pseudo-globulin and serum itself also exhibit an increase in absorption when irradiated in the presence of alkali, but euglobulin does not. Egg albumin behaves as does serum albumin.[74] If acid or alkali is added before the irradiation, the increase in absorption increases with the concentration of the added acid or alkali. The effects are much less marked when x-ray or radium irradiation is employed. However, in the presence of materials which under x-radiation fluoresce in the ultraviolet region, the effects of x-rays are similar to those of ultraviolet rays.

Wels[75] found the bluish fluorescence of serum euglobulin under ultraviolet irradiation to be increased after irradiation with unfiltered ultraviolet rays.

Spiegel-Adolf[76] found also that after removing ultraviolet-coagulated serum globulin from a dilute solution, the filtrate contained a substance, probably proteose in nature, which coagulates a sol of colloidal gold. When a concentrated solution of this substance is added to spinal fluid, the mixture simulates the fluid of cases of general paralysis in the diagnostic colloidal gold precipitation test. She also showed that, after irradiation, gelatin solutions lose their protective power for gold sols and tend instead to precipitate them.[77] Arginine, histidine, lysin and choline flocculate colloidal gold only after irradiation, whereas glycine and the cyclic amino- acids do not acquire this property even after irradiation. The ability of histamine solutions (0.00018 mg. per cc.) to precipitate gold sol is lost on irradiation, although not at the same rate at which the pharmacological properties of this compound are lost. Irradiation also destroys the protective power of thymonucleic acid which becomes, like cytosine and uracil, a gold sol precipitant. Exposures up to six hours are required, however.

It has been claimed that differences between globulins and albumins exposed to ultraviolet light for varying periods, 45 minutes, 3 hours and 6 hours, can be demonstrated by the biological reaction of Abderhalden.[78] The enzymes produced by an animal in the Abderhalden reaction after the injection of such products are claimed to be specific for the kind of protein and its exposure time. It also is claimed that irradiation increases the susceptibility of globulin but not of albumin to the action of gastric juice.

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[72] A summary is given in *Arch. Path* , **12**, 533 (1931).

[73] Spiegel-Adolf, M., and Krumpel, O., *Biochem. Z.*, **190**, 28 (1927); *Klin. Wochschr.*, **7**, 1592 (1928); *Biochem. Z.*, **197**, 197 (1928)

[74] Spiegel-Adolf, M., and Oshima, Z., *Biochem. Z.*, **208**, 32 (1929); compare Spiegel-Adolf, M., and Krumpel, O., *Ibid.*, 45, for the effects of heat on absorption.

[75] Wels, P., *Arch. ges. Physiol. (Pflüger's)*, **219**, 738 (1928).

[76] Spiegel-Adolf, M., *Biochem. J.*, **28**, 372 (1934).

[77] Spiegel-Adolf, M., *Biochem. J.*, **28**, 1201 (1934).

[78] Abderhalden, E., and Buadze, S., *Fermentforschung*, **14**, 295 (1934); *Chem. Abs.*, **28**, 6739 (1934).

Early work of Harris[79] indicated that oxygen is absorbed during the irradiation of egg albumin, casein and edestin, but not of gelatin. At the same time, the characteristic absorption maximum at 2800A disappears, at least in the case of egg albumin, according to Becker and Szendrö.[80] Hematoporphyrin and chlorophyll greatly accelerate the velocity of oxidation of plasma in light. This is true also, but to a lesser degree, of a number of dyes, such as methylene blue and eosin, and of ionic iron.[81]

Wels demonstrated[82] that the irradiation of egg albumin in an atmosphere of nitrogen leads to the production of a substance which can be readily oxidized by oxygen or by methylene blue. This converts the substance into an oxidant capable of oxidizing the yellow leucobase of the red dye, Rosindulin GG. Irradiation under decreased oxygen tension instead of under nitrogen decreases but does not entirely prevent the formation of the substance which reduces methylene blue. After irradiation in oxygen at higher tensions, the substance is produced only in the oxidant form, capable of oxidizing the leuco-rosindulin but not of reducing methylene blue. Wels concluded from these observations that irradiated skin is the source of a substance analogous to the sulfhydryl compounds and which may play a part in tissue respiration. The property of bleaching methylene blue not shown by protein irradiated in an oxygen stream may be acquired by keeping the solution for a few hours in contact with washed frog muscle or its dry powder. The dry muscle powder bleaches methylene blue very slowly; if it is irradiated in nitrogen,[83] and oxidized protein is added, the bleaching is accelerated four times. Non-irradiated protein does not act.

That the reduction-oxidation potential of solutions of egg and serum albumins is reduced by coagulation either by heat or ultraviolet light has also been observed by Nakamura.[84] Kather[85] states that ultraviolet-irradiated egg albumin forms a copper-complex which is five to ten times as active as that from the non-irradiated protein in catalyzing the oxidation of unsaturated acids.

Fibrinogen is precipitated from its solutions by irradiations. Such irradiated solutions are no longer coagulated by the toxin of *Crotalus terrificus*.[86] The action of the ultraviolet light on this globulin is inhibited by the presence of hematoporphyrin.[87]

Dried hide powder, after several weeks of irradiation by a quartz mercury arc, either in air or in a quartz tube under nitrogen, acquires a bright canary yellow color. Of the irradiated powder, 27.8 per cent dissolves in an equal weight of water at room temperature. The capacity of hide powder to combine with hemlock tannin at pH 3.8 is greatly reduced by the irradiation.[88]

Keratin, as in unbleached horn, after ultraviolet irradiation, assumes in a lead nitrate solution a deeper color than that given by the non-irradiated sample. Wool shows a similar behavior. Thus only after irradiation do bleached horn and bleached wool acquire the ability to form lead sulfide with solutions of lead salts.[89]

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[79] Harris, D. T., *Biochem. J.*, 20, 288 (1926).

[80] Becker, J. P., and Szendrõ, P., *Arch. ges. Physiol. (Pflüger's)*, 228, 755 (1931).

[81] Harris, D. T., *Biochem. J.*, 20, 280 (1926).

[82] Wels, P., *Arch. exp. Path. Pharmakol.*, 171, 480 (1933); *Chem. Abs.*, 27, 5344 (1933).

[83] Wels, P., and Hesse, R., *Naturwiss.*, 22, 648 (1934).

[84] Nakamura, Y., *J. Agr. Chem. Soc. Japan*, 11, 1101 (1935); *Brit. Chem Abs.*, **A**, 360 (1936).

[85] Kather, E., *Arch. exp. Path. Pharmakol*, 184, 645 (1937); *Brit. Chem. Abs.*, **A** (III), 253 (1937).

[86] Arthus, M., and Boshell, G., *Arch. intern. physiol.*, 30, 244 (1928); *Brit. Chem. Abs.*, **A**, 1024 (1929).

[87] Howell, W. H., *Arch. intern. physiol.*, 18, 269 (1921); *Chem. Abs.*, 16, 935 (1922).

[88] Thomas, A. W., and Foster, S. B., *J. Am. Leather Chem. Assoc.*, 20, 490 (1925).

[89] Beutel, E., and Kutzelnigg, A., *Monatsh.*, 64, 183 (1934).

It is assumed that a part of the sulfur of keratin is converted into sulfur ions under the influence of light. On the other hand, Barritt and King[90] state that on exposure to ultraviolet radiations wool loses part of its sulfur as sulfur dioxide, which may be evolved, adsorbed or oxidized to sulfuric acid. From x-ray observations, Astbury and Woods[91] state that irradiation of unstretched keratin by ultraviolet light or x-rays causes intramolecular changes analogous to those due to the action of water on stretched keratin.

It has been claimed that when gelatin is irradiated, it is altered in such a way as to lessen its tendency to swell in water. The effect is said to be proportional to the duration of illumination.[92] The solubility of the swollen gelatin in water is reduced, and the irradiated solution has the property of reducing ammoniacal silver nitrate solution, but the elementary analysis is unaffected. The presence of oxygen during the irradiation is not essential. The effects of irradiation may be lessened by careful purification of the gelatin, and it has been suggested that an iron sensitizer found in the ash may be necessary for the process. Sheppard and Houck[93] believe the underlying reaction to be of termolecular order. According to Ponthus[94] irradiation increases the electrical conductivity and decreases the optical density and viscosity of gelatin, but does not change its state of aggregation. Duce[95] finds the surface tension to be lowered and attributes this effect to a decrease in the hydration of the colloidal particles.

Insulin is not resistant to ultraviolet rays in the presence of oxygen and it cannot, therefore, be sterilized by them.[96] Variations observed in the effect of these radiations on commercial insulin preparations have been attributed to variations in their content of phenol, which protects the preparation against their action.[97] According to Ellis and Newton,[98] exposure of commercial insulin in nitrogen in a quartz tube for 19 to 48 hours destroys the active hypoglucemic substance. Substances remain which, when injected, have the property of increasing the blood sugar level. Ozone and oxygen in sunlight destroyed the hypoglucemic substance in insulin solutions but did not develop the substances producing the increase in blood sugar in one hour.[99]

Freudenberg and Wegmann[100] find that the activity of irradiated insulin can be partly restored by oxidation by hydrogen peroxide in the presence of cysteine. Irradiated egg-white inactivates insulin in an atmosphere of nitrogen. The photochemically liberated sulfhydryl groups reduce the active disulfide form of insulin to the inactive sulfhydryl form.[101] The reducing properties may be developed in protein even by therapeutic doses of irradiation.[102]

In the presence of quinones as sensitizers, hemoglobin (and also chlorophyll) absorb hydrogen under the influence of light.[103] Oxidation occurs subsequently, turning the quinones (with the exception of juglone), brown. In sunlight, hemoglobin is degraded into its decomposition products, the process being accelerated by the use of glutathione as sensitizer. Under these conditions, chlorophyll may be destroyed.[104] Lennox[105] states that in ultraviolet light, potassium iodide, but not free iodine, accelerates the conversion of hemoglobin to methemoglobin. Etioporphyrin I, when irradiated in pyridine containing sodium ethylate, alters its spectrum, a new absorption band appearing at 6360A, the red solution becoming blue and then green.[106] Oxygen is necessary for the change to occur. The solution contains etioglaucobilin and a red diketone of this substance, besides a mixture of dinuclear aldehydes, very similar to etioneoxanthomethenes. The first step in the photochemical oxidation is the addition of oxygen at several of the methine bridges of the porphyrin. The resulting peroxide isomerizes and the bridge breaks to yield an isomer of glaucobilin, which rearranges. The other products result from other rearrangements of the peroxide.

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[90] Barritt, J., and King, A. T., *J. Textile Inst.*, **20**, 151T, 159 (1929); *Brit. Chem. Abs.*, **B**, 846 (1929).

[91] Astbury, W. T., and Woods, H. J., *Phil. Trans.*, **32**, 333 (1933).

[92] Brintzinger, H., and Maurer, K., *Kolloid.-Z.*, **41**, 46 (1927).

[93] Sheppard, S. E., and Houck, R. C., *J. Phys. Chem.*, **36**, 2885 (1932).

[94] Ponthus, P., *Compt. rend.*, **196**, 1248 (1933).

[95] Duce, W., *Arch. ital. biol.*, **94**, 34 (1935); *Boll. soc. ital. biol. sper.*, **10**, 978 (1935); *Chem. Abs.*, **30**, 2454 (1936); Kronenberger, P., *Boll. soc. ital. biol.*, **9**, 1336 (1934).

[96] Cazzini, U., *Biochem. terap. sper.*, **16**, 563 (1929); *Chem. Abs.*, **24**, 917 (1930); Den Hoed, D., De Jongh, S. E., and Peek, A., *Biochem. Z.*, **205**, 144 (1929).

[97] Küstner, H., and Eissner, W., *Klin. Wochschr.*, **11**, 1668 (1932); *Chem. Abs.*, **27**, 779 (1933).

[98] Ellis, M. M., and Newton, E. B., *Am. J. Physiol.*, **73**, 530 (1925).

[99] Keeser, E., [*Arch. exp. Path. Pharmakol.*, **166**, 624 (1932); *Chem. Abs.*, **26**, 5582 (1932)] believes irradiation with green or blue light to activate insulin, although red light partially destroys its activity.

[100] Freudenberg, K., and Wegmann, T., *Z. physiol. Chem.*, **233**, 159 (1935).

[101] Kather, E., *Arch. exptl. Path. Pharmakol.*, **185**, 323 (1937); *Chem. Abs.*, **32**, 6267 (1938).

[102] Kämmerling, I., *Arch. exptl. Path. Pharmakol.*, **186**, 434 (1937); *Chem. Abs.*, **32**, 8448 (1938).

ENZYMES

Since the activity of an enzyme depends, in general, upon the integrity of its colloidal protein component, the destruction of the activity of enzymes is intimately bound up with the effects of ultraviolet upon the proteins. Since, however, there may conceivably be various prosthetic groups in the enzyme molecule which also condition its activity, the details of the destruction process may be expected to vary from enzyme to enzyme. Therefore, although most enzymes which have been tested have been found to be sensitive to ultraviolet rays, the behavior of each must be discussed separately. In many cases the activity of enzymes depends also upon the presence of specific coenzymes, and these also may be affected by radiations.[107]

It has been claimed that certain monochromatic radiations in the visible range increase the activity of catalase, pepsin, trypsin, and lipase. In no case was the enzyme activity depressed.[108]

Application of ultraviolet rays may aid in determining the unitary or non-unitary nature of certain enzymes which have the property of acting upon more than one substrate. If the activity toward each is destroyed at the same rate on irradiation of the preparation it may be assumed that but one enzyme is involved, according to Helferich and Brieger.[109] In the emulsion of almonds, the activity toward phenol β-*d*-glucoside and phenol-*d*-galactoside diminish at the same rate, suggesting that both substrates are hydrolyzed by the same enzyme. The activity toward phenol -β-*d*-glucoside, however, diminished twice as rapidly as that toward phenol α-*d*-mannoside, suggesting that different enzymes affect these substrates.[110]

Diastase. The behavior of this enzyme has been extensively studied by Pincussen. It is not destroyed by sunlight, but is inactivated by shorter ultraviolet rays. The destruction is greatest at pH 4.6 at which the enzyme also exhibits its maximum activity. The destruction is least at pH 7.0 and 7.4.[111] The rate is accelerated by the presence of iodides and inhibited by glycine and by starch, but is but little affected by sugars or by change of temperature. In the presence of dextrose, sunlight may have a slight effect. The inactivation of 0.1-per cent malt diastase acting on 1-per cent starch solution at varying pH values proceeds as a unimolecular reaction, although in the presence of 0.5 per cent of starch only the later stages of the reaction are expressed by the unimolecular rate equation. The disagreement is still more marked in the presence of 0.25 per cent of starch. A 0.2-per cent solution of the enzyme gives complex results in the presence of either 1-, 0.5- or 0.25-per cent starch solutions.[112]

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[103] See also Gouzon, B., *Ann. physiol. physicochim. biol.*, **11**, 388 (1935).

[104] Kögel, G., *Strahlentherapie*, **42**, 379 (1931); *Brit. Chem. Abs.*, **A**, 634 (1932).

[105] Lennox, F. G., *Australian J. Exptl. Biol. Med. Sci.*, **13**, 193 (1935); *Brit. Chem. Abs.*, **A**, 92 (1936).

[106] Fischer, H., and Herrle, K., *Z. physiol. Chem.*, **251**, 85 (1938).

[107] An early attempt to classify enzymes in accordance with their sensitivity to ultraviolet under various conditions was made by Agulhon, H., *Compt. rend.*, **153**, 979 (1911).

[108] Keeser, E., *Arch. exp. Path. Pharmakol.*, **164**, 626 (1932); *Chem. Abs.*, **26**, 3269 (1932); note also Collier, H. B., and Wasteneys, H., *Australian J. Exp. Biol. Med. Sci.*, **9**, 89 (1932); *Chem. Abs.*, **27**, 2164 (1933).

[109] Helferich, B., and Brieger, G., *Z. physiol. Chem.*, **221**, 94 (1933); Helferich, B., Rohr, H., and Günther, E., *Ibid.*, 90.

[110] Note also Hill, K., *Ber. für Handlung. Sachs. Akad. Wiss. Leipzig, Math. Phys. Klasse*, **86**, 115 (1934); *Chem. Abs.*, **28**, 5843 (1934).

Phosphate solutions ($6M$) protect malt diastase and the maltase of pancreatin from inactivation by ultraviolet rays, but less dilute solutions are less effective. Similar results are given by acetate solutions of the same pH. In the presence of a phosphate buffer, with or without the addition of sodium chloride, the protective action is at a maximum at pH 6.64.[113] Ammonium, potassium and lithium chlorides, potassium bromide and sodium fluoride protect Taka-diastase to varying degrees, the effects being more marked in dilute solutions of these salts than in more concentrated ones. Potassium and sodium nitrates and nitrites give similar results but do not show the same varying effects at different temperatures.

Lüers and Lorinser[114] found the inactivation of malt amylase by ultraviolet rays followed neither the mono- nor bi-molecular reaction equations or the Schutz law. The temperature coefficient is 1.30 between 20 and 30°C.

Pincussen[115] believed also that in alkaline solutions, irradiation increases the action of salivary and Taka-diastases, pancreatic diastases showing a similar but very much less marked response.

During the progressive purification of diastase from the pancreas, the sensitivity toward ultraviolet rays progressively increases.[116] Diastase which had been rendered almost inactive by irradiation could be partly reactivated by the addition of small quantities of non-irradiated diastase. Since this effect is not obtained in the case of heat inactivation, the mechanisms of the two modes of inactivation were thought different.[117]

Although Kawakami[118] was unable to confirm the inactivation of Taka-diastase by ultraviolet rays, Thompson and Hussey[119] found the inactivation of amylase to follow a unimolecular course for 88 per cent of the process. Similar results were recorded for Taka-diastase in 0.1-per cent solution by Yamashiki.[120] The influence of the voltage at which the mercury arc was operated upon the value of the monomolecular rate constant was determined by Thompson and Tennant[121] for pancreatin solutions. With 4 amperes and a potential of 75 volts, 0.02-per cent pancreatin solution at pH 6.7 gave a constant of 0.259. With 70 volts across the lamp it was reduced to 0.172 and with 80 volts it was raised to 0.302. The protective action of added dog serum on the stability of the solutions could be accounted for by internal filtering without the necessity of assuming for the serum a specific negative catalytic action.

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[111] Pincussen, L., *Biochem. Z.*, **134**, 459 (1923); *J. Soc. Chem. Ind.*, **42A**, 370 (1923).

[112] Pincussen, L., and DiRenzo, F., *Biochem. Z.*, **144**, 366 (1924).

[113] Pincussen, L., *Biochem. Z.*, **144**, 372 (1924); see also Terroine, E. F., and Bonnet, R., *Bull. soc. chim. biol.*, **9**, 982 (1927); *Chem. Abs.*, **22**, 1169 (1928).

[114] Lüers, H., and Lorinser, P., *Biochem. Z*, **144**, 212 (1924).

[115] Pincussen, L., *Biochem Z*, **152**, 406 (1924).

[116] Pincussen, L., *Fermentforschung*, **8**, 181 (1925); *Biochem. Z.*, **171**, 1 (1926). Note also Kambayashi, Y., *Biochem. Z*, **203**, 334 (1928).

[117] Pincussen, L., and Oya, T., *Biochem Z*, **207**, 410 (1927).

[118] Kawakami, T., *J. Pharm. Soc. Japan*, **49**, 361 (1929); *Chem. Abs.*, **23**, 4238 (1928).

[119] Thompson, W. R., and Hussey, R., *J. Gen. Physiol*, **15**, 9 (1931).

[120] Yamashiki, H., *Acta Schol. Med. Univ. Imp. Kyoto*, **16**, 365 (1934); *Chem. Abs.*, **28**, 4759 (1934).

[121] Thompson, W. R., and Tennant, R, *J. Gen. Physiol.*, **18**, 675 (1935).

Sensitizers like eosin, sodium anthraquinone disulfonate and sodium dichloroanthracene disulfonate aid various photochemical processes but have only a depressing effect upon the inactivation of Taka-diastase by ultraviolet light. Potassium ions increase the effects of light and decrease the rate of heat inactivation; the reverse is true of the calcium ion.[122]

Diastase also may be protected from the action of ultraviolet light by the presence of asparagine, anilinoacetic acid, ammonium citrate, gelatin or tyrosine, probably by internal filtering.[123]

Hutchinson and Ashton[124] found that full ultraviolet irradiation retards the ability of both salivary and malt diastases to produce dextrin and sugars from starch in an inverse relation to the intensity of the light used. They report also that green light had a somewhat similar effect on salivary diastase, but that both salivary and malt preparations were stimulated in their activity by either red-yellow or near ultraviolet light. Apparent differences of the rates of production of dextrins and of maltose by malt diastase during irradiation with various monochromatic radiations led them to suspect the presence of different enzymes in the preparation.

Tang and Sung[125] find fully germinated malt unaffected by ultraviolet rays, although malt which had just begun to germinate lost its activity on irradiation.

Sucrase. Preparations of this enzyme exhibit an absorption band with its maximum at about 2700A, attributed to the presence of tryptophane in the protein of the enzyme. Addition of this amino- acid protects[126] the enzyme from inactivation by ultraviolet light. Yeast gums also present in the preparations have but very little absorption at 2700A.

Although yeast autolyzates are almost uninjured by irradiation for two hours, sucrase preparations of a high degree of purity were inactivated within twenty to thirty minutes.[127] The pH had but slight effect on the course of inactivation. The curve was linear during the earlier part of the reaction, but fell off later. In the presence of molecular oxygen, there was an apparent activation during the first ten minutes of irradiation, this being ascribed to oxidation of inhibiting substances assumed to be present in the preparations employed. No reactivation could be obtained by the addition of tryptophane or yeast gums. On the contrary, these additions, particularly the yeast gums, hasten the postinactivation which occurs on standing in preparations which have been previously irradiated for ten minutes.[128]

Recently, the activating effects of very brief irradiation (3650 and 3660A), of 5 minutes for autolyzates or half that long for dialyzates, was again noted by Gorbach with Ruess.[129] The effect is observed after the irradiated solutions have stood a short while, increasing to a maximum and then declining with time. Repeated short irradiations give greater activation than a single longer one.

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[122] Kumanomidoh, S., with Pincussen, L., *Biochem. Z.*, **195**, 79 (1928).

[123] Banerjee, S., and Sen, H. K., *J. Indian Chem. Soc.*, **12**, 379 (1935); *Chem. Abs.*, **30**, 113 (1936).

[124] Huchinson, A. H., and Ashton, M. R., *Canadian J. Research*, **9**, 49 (1933); *Chem. Abs.*, **27**, 5353 (1933).

[125] Tang, T.-H., and Sung, T.-T., *J. Chinese Chem. Soc.*, **5**, 174 (1937); *Chem. Abs.*, **31**, 6405 (1937).

[126] Gorbach, G., and Lerch, K., *Biochem. Z.*, **219**, 122 (1930); *Chem. Abs.*, **24**, 2769 (1930); *Biochem. Z.*, **235**, 259 (1931); *Chem. Abs.*, **25**, 4565 (1931).

[127] Gorbach, G., and Pick, H., *Monatsh.*, **61**, 29 (1932); *Chem. Abs.*, **27**, 110 (1933).

[128] Gorbach, G., and Kimovec, D., *Monatsh.*, **61**, 39 (1932); *Chem. Abs.*, **27**, 110 (1933).

[129] Gorbach, G., with Ruess, H., *Biochem. Z.*, **271**, 338 (1934); *Chem. Abs.*, **29**, 2186 (1935); *Biochem. Z.*, **280**, 213 (1935); *Chem. Abs.*, **30**, 120 (1936).

Albers and Meyer[180] doubt the evidence of Gorbach that tryptophane is the carrier of the enzyme activity, since, although tryptophane could be detected in the purest preparations of this enzyme, its content was not proportional to the enzyme activity. The observed increase in the absorption, particularly of the longer wave-lengths, was attributed to an aggregation of the colloidal carrier accompanied by an alteration or masking of the active groups.[180a]

Ultraviolet light retards the action of phosphatase from tuberculous lymph glands of rabbits on calcium fructose mono- and sucrose-phosphate, but not on calcium α-glycerophosphate. In the presence of eosin, sunlight also diminished the activity of the phosphatase.[181] Collier and Wasteneys[182] find that plasma phosphatase may be destroyed by ultraviolet and by visible light.

Lipase. There have been recent claims that monochromatic radiations of long wave-length stimulate the activity of lipase. This effect, at least that on the action of the lipase of autolyzed yeast on castor oil, is said to be decreased when light of greater intensities is used.[183] Ultraviolet rays, however, inactivate lipase.[184] Similar observations have been recorded on the destruction of lipase in the blood serum of rabbits or guinea pigs. The proteins in the serum exert a protective action and the effects are greater when part of the protein content is removed.[185]

Irradiation of dry powdered seeds of *Ricinus communis* does not affect their lipase activity.[186]

Proteinases. That pepsin solutions can be inactivated by ultraviolet rays by a monomolecular reaction was observed by Hussey and Thompson and later confirmed by Gates.[137] Northrop[138] found the loss of activity of his crystalline preparations caused by either ultraviolet rays or radium to be exactly proportional to the rate of loss of proteins by denaturation. This was evidence supporting the view that the enzyme is a crystalline protein and not merely some simpler substance carried by the protein, or at any rate that the protein molecule is itself responsible for the enzyme activity of the preparation. The rate of inactivation varied with the pH of the solution; it had its maximum value at pH 2. Uehara places it at pH 1.4.[139]

The preparations exhibit an absorption band between 2600 and 2900A. At low temperatures this may be resolved into a number of sharp narrow bands.[140] Gates found in a series of experiments with monochromatic ultraviolet light that the destruction of pepsin by different wave-lengths agrees in general with its absorption spectrum. Thus, by plotting the reciprocals of the energies required for various wave-lengths to produce the same degree of inactivation there is obtained a curve, the destruction spectrum, which is similar in form and location to the absorption spectrum. During the process of irradiation, an increase in absorption occurs at wave-lengths other than that of the maximum absorption. Thus the minimum in the absorption spectrum at about 2500A was gradually lost and the long wave-length leg of the absorption curve also showed a very considerable increase in absorption.[141] A protective action by proteins also has been observed in the case of this enzyme by Banerjee and Sen.[142]

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[180] Albers, H., and Meyer, I., *Z. physiol. Chem.*, 228, 122 (1934).

[180a] This, however, may be not necessarily the case since similar increases in absorption during brief irradiation periods have been observed in crystalline pepsin and uracil solutions where there is no possibility of the presence of a carrier of high molecular weight.

[181] Horii, I., *Arb. Inst. Univ. Kyoto,* III C, 62, 1931; *Brit. Chem. Abs.*, A, 874 (1932).

[182] Collier, H. B., and Wasteneys, H., *Australian J. Exp. Biol. Med. Sci.*, 9, 89 (1932); *Chem. Abs.*, 27, 2164 (1933).

[183] Murakami, R., *J. Agr. Chem. Soc. Japan*, 12, 709 (1936); *Chem. Abs.*, 31, 1436 (1937). This author made similar observations on yeast amylase, proteinase and urease, *J. Agr. Chem. Soc. Japan*, 12, 175, 180 (1936); 12, 151; 13, 46 (1937).

[184] Takayama, T., *Bull. Agr. Chem. Soc. Japan*, 5, 71 (1929); *Chem. Abs.*, 25, 123 (1931).

[185] Pincussen, L., and Hayashi, S., *Biochem. Z.*, 195, 196 (1928).

[186] Cousin, E., and Creach, P., *Bull. soc. pharm. Bordeaux*, 75, 12 (1937); *Chem. Abs.*, 31, 6681 (1937).

[137] Gates, F. L., *J. Gen. Physiol.*, 17, 797 (1933-4); 18, 265 (1934).

[138] Northrop, J. H., *J. Gen. Physiol.*, 17, 359 (1934).

[139] Pincussen, L., and Uehara, K., *Biochem. Z.*, 195, 87 (1928).

[140] Lavin, G. I., Northrop, J. H., and Taylor, H. S., *J. Am. Chem. Soc.*, 55, 3497 (1933); 57, 874 (1935).

Trypsin also is inactivated by ultraviolet but not by visible rays. The effect is maximal in the absence of iodides of the alkalies or alkaline earths.[143]

The eosin-sensitized photochemical destruction of rennet by visible light follows a unimolecular course, the rate constant being independent of the time of irradiation until 60 per cent of the enzyme has weakened. Its value increases with the concentration of the enzyme and is proportional to the intensity of illumination.[144]

Purified tyrosinase can be injured by irradiation, according to Pincussen and Hammerich.[145] It is suggested that this may in some manner be concerned with the formation of melanins from tyrosine or related substances in irradiated skin. Alverdes [146] believed that yellow rays promote the activity of the tyrosinase of the larvae of *Cyclops viridis*.

The destruction and absorption spectra of urease in the ultraviolet region are believed coincident by Kubowitz and Haas.[147] According to Pincussen and Kato,[148] sunlight acting on urease solutions at pH 6.4 diminished the activity both of the active constituents and of a so-called "stable Component-X." Potassium hydrogen phosphate at pH 5.6 affords partial protection to the active component, but even in darkness the activity of the other constituents is decreased by phosphate Ultraviolet irradiation destroys the active enzyme both in the presence and absence of phosphate, but does not have such a marked effect as sunlight in inhibiting Component X. Collier and Wasteneys [149] found that impure urease may be destroyed not only by ultraviolet but also by infrared rays. The quantity of ammonia produced by soy urease is said, however, to increase with the intensity of monochromatic light of various wave-lengths tested by Murakami.[150] Crystalline urease is rapidly destroyed by ultraviolet irradiation and cannot be reactivated by reducing agents or tissue extracts. Irradiated urease produces no antiurease when injected into animals.[151]

Ultraviolet rays decrease the activity of animal rennet, although they have no effect on the rennet derived from plants, such as thistle blossoms.[152] Ultraviolet light destroys thrombin, but prothrombin is more resistant, according to Cekada.[153]

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[141] Note also Collier, H. B., and Wasteneys, H., *Australian J. Exp. Biol. Med. Sci.*, **9**, 89 (1932); *Chem. Abs.*, **27**, 2164 (1933).

[142] Banerjee, S., and Sen, H K., *J. Indian Chem. Soc*, **12**, 740 (1935); *Chem Abs.*, **30**, 2581 (1936)

[143] Pincussen, L., and Klissiunis, N., *Biochem. Z.*, **152**, 416 (1924); Pace, J., *Ibid.*, **240**, 490 (1931).

[144] Schmidt-Nielsen, S, and Fjermeros, E., *Compt. rend trav lab. Carlsberg, Sér. chim.*, **22**, 473 (1938); *Chem. Abs.*, **32**, 6266 (1938).

[145] Pincussen, L., and Hammerich, T., *Biochem Z*, **239**, 273 (1931).

[146] Alverdes, F., *Archiv Entwickl. Organ.*, **47**, 375 (1921)

[147] Kubowitz, F., and Haas, E., *Biochem. Z.*, **257**, 337 (1933).

[148] Pincussen, L., and Kato, N, *Biochem. Z.*, **142**, 228 (1923)

[149] Collier, H. B., and Wasteneys, H., *Australian J. Exp. Biol. Med. Sci.*, **9**, 89 (1932); *Chem. Abs.*, **27**, 2164 (1933).

[150] Murakami, R. J., *Agr. Chem. Soc. Japan*, **13**, 439 (1937); *Chem Abs.*, **32**, 1723 (1938).

[151] Pillemer, L., Ecker, E. E., Myers, V. C., and Muntwyler, E., *J. Biol. Chem.*, **123**, 365 (1938).

[152] Christen, C., and Virasoro, E., *Lait*, **15**, 354, 496 (1935); *Chem. Abs.*, **29**, 5134 (1935).

[153] Cekada, E. B., *Am. J. Physiol.*, **78**, 512 (1926)· For the behavior of baicalinase, see Miwa, T., *Acta Physicochim.*, **9**, 89 (1936); *Chem. Abs.*, **30**, 8272 (1936), and for β-glucuronosidase, Oshima, G., *J. Biochem. (Japan)*, **23**, 305 (1936); *Chem. Abs.*, **30**, 4882 (1936).

Enzymes Concerned with Respiration. Ito[154] noted that catalase has two absorption bands at 4060 and 2660A, the first corresponding to the absorption band of hemin. Quite different was the earlier statement by Kuhn, Hand and Florkin[155] that the absorption spectrum of catalase shows three bands at 6290, 5400 and 5000A, in contrast to the continuous visible absorption of peroxidase. Zeile and Hellström[156] also gave absorption spectral evidence that liver catalase contained a porphyrin iron complex, the carrier of the catalase function.

Blood catalase is more readily destroyed in dilute than in stronger solutions, and the most rapidly at pH 6.81, the optimum for its activity.[157] The addition of salts protected the catalase from the action of light. In the case of potassium iodide, the results were complicated by the action of the iodine liberated by the light. Morgulis and Schumacher[158] found that the process proceeds at a uniform rate at pH 6.28. At more acid or alkaline reactions, the initial rate of inactivation diminishes considerably with the lapse of time. At pH 11, this effect is so marked that the enzyme may be said to be actually stabilized against the radiations.

Spectrographic determinations have been used in an original manner by Stern[159] in following the formation of intermediate compounds during the action of this enzyme. He noted that purified catalase solutions show, in addition to the hematin absorption in the visible regions, ultraviolet bands due to the protein carrier. These varied with the source from which the catalase had been prepared. Irradiation from a mercury lamp inactivated the enzyme and changed its fluorescence from yellow-green to blue-green. This effect did not occur if a nickel oxide filter was interposed.

Califano[160] believed that by irradiation with blue mercury lines 4050 to 4360A, the intensity of catalase activity is decreased. There is little action by 4920A and none by 5460 and 5780A. The compound of catalase and carbon monoxide is decomposed by the 4050A line and less so by that at 4920A.

Ultraviolet irradiation of yeast cells has been claimed to increase their catalase activity several times.[161] After 16 to 18 hours it increases 300 per cent in *Saccharomyces ellipsoideus*, 1000 per cent in *Torula rosa* and 2500 per cent in *Torula colliculosa*. However, there was only a slight increase in the case of silkworm eggs.[162]

Green-colored rice may be decolorized by sunlight, but not by ultraviolet rays. During this process, the catalase and peroxidase activities decreased remarkably, but this also did not occur when ultraviolet rays were used.[163]

From absorption data, Kuhn, Hand and Florkin[164] believed it probable that the active group in peroxidase is an iron porphyrin compound. The absorption appeared to be continuous and located in the visible region. Peroxidase inhibited by carbon monoxide could not be reactivated by light. According to Pincussen and Hammerich[165] this enzyme is destroyed also by the rays of the quartz mercury arc, the loss of activity being almost proportional to the light intensity. Aside from the fact that the greatest destruction occurs in acid solution, the pH has relatively little influence upon the process.

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[154] Ito, R., *J. Biochem., Japan,* **22,** 139 (1935); *Chem. Abs.,* **29,** 8025 (1935).

[155] Kuhn, R., Hand, D. B., and Florkin, M., *Z. physiol. Chem.,* **201,** 255 (1931).

[156] Zeile, K., and Hellström, H., *Z. physiol. Chem.,* **192,** 171 (1930). See also Stern, K. G., *J. Biol. Chem.,* **121,** 561 (1937).

[157] Pincussen, L., and Seligsohn, F., *Biochem. Z.,* **168,** 457 (1926).

[158] Morgulis, S., and Schumacher, L., *J. Biochem.,* **86,** 75 (1930).

[159] Stern, K. G., *Nature,* **136,** 335 (1935); **136,** 302 (1935); *Z. physiol. Chem.,* **212,** 207 (1932); **219,** 105 (1933).

[160] Califano, L., *Naturwiss.,* **22,** 249 (1934); *Chem. Abs.,* **28,** 5478 (1934).

[161] van Euler, H., and Günther, G., *Z. physiol. Chem.* **220,** 69 (1933); *Chem. Abs.,* **27,** 5343 (1933). Variations in intensity are believed more significant than variations in wave-length by Murakami, R., *J. Agr. Chem. Soc. Japan,* **13,** 429, 435 (1937); *Chem. Abs.,* **32,** 1723 (1938).

[162] Yamafuji, K., *Enzymologia,* **1,** 120 (1936); **2,** 147 (1937); *Chem. Abs.,* **30,** 7600 (1936); **32,** 9101 (1938). Similar observations on Spirogyra were recorded by Burge, W. E., and Burge, E. L., *Bot. Gaz.,* **77,** 220 (1924).

[163] Kondo, M., and Okamura, T., *J. Sci. Agr. Soc. Japan, No 327,* 67 (1931); *Chem. Abs.,* **25.** 5689 (1931).

[164] Kuhn, R., Hand, D. B., and Florkin, M., *Z. physiol. Chem.,* **201,** 255 (1931).

An enzyme of the liver which oxidizes ethyl alcohol is also inactivated by ultraviolet light.[166] Keilin[167] believes the indophenol oxidase system of yeast cells which has been impaired by combination with carbon monoxide may be regenerated by the dissociating action of light.

The xanthine oxidase obtainable from milk may be inactivated by sunlight, ultraviolet light or radium, according to Toyama.[168] Its absorption band has a maximum at 2790A; this is shifted toward greater wave-lengths in an alkaline medium.[169]

The action of a specific dehydrogenase in decolorizing methylene blue in the presence of alcohol as the hydrogen donor in an evacuated Thunberg tube may be accelerated by irradiation with a quartz mercury lamp.[170] According to von Euler and Klussmann,[171] this is not due to a rise in temperature, to a photochemical action on the dye alone, or to photoöxidation of the yeast extract. The effect is absent if a succino-dehydrogenase or liver extract system is used, but the effect is observed when apozymase and cozymase are used instead of yeast. von Euler, Hellström and Brandt[172] believe that the reduction of methylene blue in a dehydrase-alcohol system is accelerated by red light. A photoreduction of methylene blue likewise takes place in the absence of enzymes in the presence of alcohol as the hydrogen donor. The number of reduced dye molecules varied from one to 6000 to one to 35 quanta under various conditions with red and with ultraviolet light. At pH 5.1, the reduction is one hundred times as fast as at pH 7. The reduction is accelerated by ferrous ions. The irradiated dye fluoresces; a single band appears at 6780 to 6800A.

The dehydrogenase of beef liver represents a complex system in which, besides glucose and the enzyme itself, there are also present a coenzyme and a flavin-enzyme. Adler and von Euler[173] found that green and blue light did not affect the reaction velocity, but a red filter (675 to 645 mμ), which corresponds to the absorption maximum of methylene blue, was effective in activating the system. This means that the photoactivation occurs upon the dye. Illumination of the complete system with visible light doubles the reaction velocity. In the absence of flavin, the reaction proceeds normally if light is supplied, so that the flavin does not participate in the light activity. Inhibition by copper occurs in light or darkness and in the presence or absence of flavin, so that it must represent a direct effect upon the dehydrogenating enzyme. That cozymase is an indispensable component of the system shows it to be functionally interdependent with dehydrogenase. When a constant light intensity is used, the speed of inactivation decreases with increasing cozymase concentration.[174] Cozymase differs from the coenzyme of the Warburg dehydrogenase in that the former but not the latter can be destroyed in solutions as concentrated as one mg. per cc.

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[165] Pincussen, L., and Hammerich, T., *Biochem. Z.*, **241**, 384 (1931).

[166] Mizusawa, H., *J. Biochem. Japan*, **18**, 243 (1933); *Chem. Abs.*, **28**, 794 (1934).

[167] Keilin, D., *Nature*, **119**, 670 (1927).

[168] Toyama, J., *Fukuoka-Ikwadai Gaku-Zasshi*, **26**, 1483 (1933); *Chem. Abs.*, **28**, 7279 (1936).

[169] Ito, R., *J. Biochem. Japan*, **22**, 139 (1935); *Chem. Abs.*, **29**, 8025 (1935).

[170] Krestownikoff, A. N., *Skand. Arch. Physiol.*, **52**, 199 (1927); *Brit. Chem. Abs.*, **A**, 445 (1928).

[171] von Euler, H., and Klussmann, E., *Naturwiss.*, **22**, 777 (1934); von Euler, H., *Arkiv Kemi, Mineral Geol.*, **11B**, 45 (1934).

[172] von Euler, H., Hellström, H., and Brandt, K., *Naturwiss.*, **23**, 486 (1935).

[173] Adler, E., and von Euler, H., *Z. physiol. Chem.*, **232**, 6, 10, 16 (1935).

Junghagen[175] finds the dehydrogenases of pyruvic and glycerophosphoric acids to be rapidly destroyed by ultraviolet light. In the range between pH 6 and 8, succinodehydrogenase is also injured by ultraviolet light, but the destruction is not so rapid in acid solutions.[176] Exposure to ordinary light for an hour also causes injury, but exposure for only half an hour merely stimulates the activity of the enzyme.

Warburg[177] made extensive use of irradiation and spectrographic methods in his investigations of his new hemin-containing respiratory enzyme.

He found its compound with carbon monoxide to be dissociable by light; and, by quantitative determinations of the intensities of various wave-lengths required to produce a given amount of destruction, determined the absorption spectrum of the carbon monoxide compound of the enzyme.[178] Irradiation of yeast cells with equal intensities of monochromatic light of various wave-lengths caused an increase in the rate of respiration of the cells. By plotting this effect against the wave-lengths, he obtained a curve of the absorption of light by the hemin of the enzyme. The spectrum of the respiratory enzyme so obtained is similar in shape to the absorption curve of the carbon monoxide compound of reduced hemin. The maximum of the latter curve is, however, at 408 mμ, and that of the respiratory enzyme is at 436 mμ. This discrepancy is accounted for by the assumption that the respiratory enzyme exists in the solid state adsorbed on the surface of the cells.

In the course of these investigations the absorption spectra of carbon monoxide, iron carbonyl, pyridine-hemin, and the compound of carbon monoxide and ferrocysteine were examined These comparative absorption spectra show not merely that the iron carbonyl group is a part of the respiratory enzyme but also that it is attached to a hemin-like molecule The absorption curve for the carbon monoxide-ferrocysteine compound is quite different.[179] Warburg, Negelein and Christian[180] found carbon monoxide-hemoglobin in carbylamine solutions to be the most light-sensitive carbon monoxide-iron-porphyrin compound then known.

In tissue sections, a blue fluorescence in Wood's light due to proteins gives way on continued irradiation to a red fluorescence characteristic of free porphyrin liberated from any complexes present by photolysis.[181]

A respiratory enzyme derived from the retina has an absorption spectrum identical with that of the enzyme derived from yeast.[182] The respiratory enzyme differs from cytochrome. A new yellow oxidation enzyme is also obtainable from bottom yeast.[183] Its absorption spectrum has three bands, two of which, at 465 and 495 mμ, are in the long wave-length range.[184] The enzyme has an active group, a reversible yellow pigment, bound to a colloidal protein carrier. The active group can be split from the protein by aqueous methanol. It fluoresces green and is catalytically inactive, but the light absorption in the visible range is almost unchanged It has two bands in the ultraviolet at 2700 and 3500A, and also one at 4450A.[185] When irradiated in dilute alkaline solution, the active component, after acidification, becomes soluble in chloroform. It yields a crystalline derivative, $C_{13}H_{12}N_4O_2$, from which it is possible to obtain urea and a compound, $C_6H_{10}N_2O_2$.[186] Theorell[187] has recently found the yellow coenzyme portion obtained after separation from the protein to consist of a flavine esterified with phosphoric acid and therefore related to the vitamin B_2 of the German workers.[187a]

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[174] von Euler, H., and Schlenk. *Arkiv Kemi, Mineral Geol.*, **12B**, No. 19 (1936).

[175] Junghagen, S., *Skand. Arch Physiol*, **54**, 115 (1928); *Chem. Abs.*, **22**, 4549 (1928).

[176] Pincussen, L., and Roman, W., *Biochem. Z*, **229**, 281 (1930).

[177] Warburg, O, *Naturwiss*, **16**, 345 (1928); Warburg, O., and Negelein, E., *Naturwiss.*, **16**, 856 (1928); *Biochem. Z.*, **202**, 202 (1928).

[178] Warburg, O, and Negelein, E., *Biochem. Z.*, **214**, 64 (1929).

[179] *Cf.* also Cremer, W., *Biochem. Z.*, **194**, 231 (1928); Krebs, H. A., *Ibid.*, **193**, 347 (1928). For the splitting by light of the carbon monoxide-ferroglutathione compound, see Kubowitz, F., *Biochem. Z.*, **282**, 277 (1934).

[180] Warburg, O, Negelein, E., and Christian, W., *Biochem. Z*, **214**, 26 (1929).

[181] Thomas, J., *Compt. rend. soc. biol.*, **125**, 386 (1937); *Chem. Abs.*, **31**, 6681 (1937).

[182] Warburg, O., and Negelein, E., *Biochem. Z.*, **214**, 101 (1929).

[183] Warburg, O., and Christian, W., *Biochem. Z.*, **254**, 438 (1932).

[184] Warburg, O., and Christian, W., *Naturwiss.*, **20**, 980 (1932); Kubowitz, F., and Haas, E., *Biochem. Z.*, **255**, 247 (1932).

[185] *Biochem. Z.*, **258**, 496 (1933); **263**, 228 (1933); **266**, 377 (1933).

Bénard, Biancani, and Biancani[188] observed that ultraviolet light dissociates the compound of carbon monoxide with hemoglobin.

Warburg and Christian[189] find that the irradiation of one microgram of their hydrogen-transferring coenzyme in 1 cc. of water with a quartz lamp destroys its catalytic activity in fifteen minutes. In a glass tube or with a solution a thousand times as concentrated, there is no measurable destruction in this time. The time required for the half destruction by an intensity of one calorie per square meter per minute (calculated from data obtained at other intensities) increases with the wave-length. It is 520 times as large at 2830A as at 1860A. From an analysis of the data, the conclusion is drawn that not all of the light absorbed, but only that absorbed by a special group in the coenzyme, brings about its destruction.

The work on the relation of ultraviolet light to the respiratory enzymes has been extensively reviewed by Wynd and Reynolds.[190]

HORMONES[191]

Künster[192] claims that the actions of various plant hormones are materially affected by irradiation.

The effects of ultraviolet light on insulin have been discussed in connection with the proteins. Adrenaline, according to Keeser,[193] is activated by red and green light and inhibited by blue light. Pennetti[194] states that, in the presence of eosin, adrenalin may be inactivated by sunlight. Some protective power is exerted against this action by pyrogallol, hydroquinone and resorcinol, but not by gelatin, egg albumin, Witte's peptone or glucose. Absorption data for adrenaline and ephedrine have been given by Marchlewski and Skarzynski,[195] who find that the stereoisomers of these products have identical absorption spectra.

The rate of oxidation of commercial adrenaline solutions with hydrogen peroxide and in light is independent of the pH, but in pure solutions of the hydrochloride an increase in rate with increase in pH can be observed. The intensity of the photoöxidation depends on the intensity and wave-lengths of the light employed; irradiation with ultraviolet light alone is said to cause less change than when both visible and invisible rays are used.[196]

Ephedrine solutions are unstable in sunlight, benzalephedrine being one of the chief decomposition products.[197] It was claimed by Terata and Ito[198] that adrenalin gains in potency (depression of intestinal motility, stimulation of uterus and vasoconstrictor action) after ultraviolet irradiation or after artificial light treatment. Ten "sunlight units," however, decreased its action. Verda, Kneer and Burge[199] find 1 : 15,000 solutions to lose their pressor effect after quartz lamp treatment. Haddock[200] states that the effects are not marked and involve mainly racemization and slight oxidation. Ewing[201] finds the physiological activity of adrenalin solutions to be completely destroyed by exposure to ultraviolet light. The decomposition products, which have no pressor action, are similar to those formed by the action of hydrogen peroxide. The activity of solutions of synephrine salts and of *p*-hydroxyphenylpropanolamine is markedly increased by moderate, but destroyed by excessive, irradiation. The activity of solutions of synephrine base is not changed by irradiation.[202]

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[186] See also Warburg, O., and Haas, E., *Naturwiss.*, **22**, 20 (1934).

[187] Theorell, H., *Biochem Z.*, **278**, 263 (1935).

[187a] (See Chapter 42.)

[188] Bénard, H., Biancani, E., and Biancani, H., *Compt. rend. soc. biol.*, **92**, 1031 (1925); *Chem Abs.*, **19**, 3278 (1925).

[189] Warburg, O., and Christian, W., *Biochem. Z*, **282**, 221 (1935).

[190] Wynd, F. L., and Reynolds, E. S., *Ann. Mo. Botan. Gardens*, **22**, 771 (1935).

[191] It has been proposed to treat glands of internal secretion with ultraviolet light in order to render them or their extracts increasingly active. Eichelbaum G., and Altenburg, J., British P. 275,183, June 21, 1927; *Brit. Chem. Abs.*, **B**, 874 (1928)

[192] Küstner, H., *Deut. Med. Wochschr.*, **58**, 625 (1932); *Chem. Abs*, **26**, 4831 (1932).

[193] Keeser, E., *Arch. exp. Path. Pharmakol.*, **166**, 624 (1932).

[194] Pennetti, G., *Arch. sci. biol.*, **9**, 398 (1927); *Chem Abs*, **21**, 3678 (1927).

[195] Marchlewski, L., and Skarzynski, B., *Bull. intern. acad. Polonaise*, **A**, 241 (1929); *Chem. Abs.*, **24**, 873 (1930).

[196] Vacek, T., *Compt. rend soc biol.*, 109, 583 (1929); *Chem. Abs.*, **25**, 1330 (1931).

[197] Moore, E. E., and Moore, M. B., *Ind. Eng. Chem.*, **23**, 21 (1931).

Prolan is inactivated by ultraviolet rays. Zondek and von Euler[203] believed the thermal stability so similar to the ultraviolet stability as to support the view that prolan is a catalyst of enzymic nature. The absorption maximum for follicular hormones lies at 2800 to 2850A.[204] Concentrates of the oxytocic hormone of the pituitary glands are inactivated by ultraviolet rays.[205] The same is true of the hormones of the ovarian follicles and placenta, the destruction probably being by oxidation.[206]

The Schering-Kahlbaum Co.[207] propose the ultraviolet irradiation of extracts of germinal gland hormones.

When human thyroid gland pulp is subjected to ultraviolet irradiation, iodine ions separate to the extent of 0.5 to 2.7 per cent of the total iodine content.[208] Westra and Hunter[209] exposed finely hashed non-goitrogenic cabbage in thin layers at 50 cm. from a mercury-vapor lamp for thirty to 120 minutes. Rabbits fed exclusively on this cabbage for twelve weeks did not develop goitre.

Secretin is quickly inactivated by ultraviolet irradiation. The absorption of ultraviolet light is thereby increased, probably because of the absorption of aldehydes formed by an extensive decomposition of the molecule. All the nitrogen is freed as ammonia.[210] Although secretin is destroyed, the villikinin in extracts from the intestinal mucosa is not; this favors the independent nature of these substances.[211]

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[198] Terata, B., and Ito, R , *Folia Pharmacol. Japon.*, **12**, No. 1, 74; No 2, 125 (1931), *Chem. Abs.*, **25**, 3127, 5708 (1931); *Manshu Igaku Zasshi*, **26**, 619, 863 (1937); *Chem. Abs.*, **32**, 8453 (1938).

[199] Verda, D. J., Kneer, L., and Burge, W. E., *J. Pharmacol.*, **42**, 383 (1931); *Chem Abs.*, **25**, 5935 (1931). See also Ewing, P. L., Blickensdorfer, P., and McGuigan, H , *J. Pharmacol.*, **43**, 125 (1931); *Chem. Abs.*, **26**, 1004 (1932).

[200] Haddock, L. A., *Quart. J. Pharm. Pharmacol.*, **6**, 496 (1933); *Chem Abs.*, **28**, 1137 (1936).

[201] Ewing, P. L., *J. Lab. Clin. Med.*, **20**, 16 (1934); *Chem. Abs.*, **29**, 2233 (1935).

[202] See also Higgins, J. A , Ewing, P. L., and McGuigan, H. A., *J. Pharmacol* , **44**, 353 (1932); *Chem. Abs* , **26**, 3302 (1932).

[203] Zondek, B., and von Euler, H., *Skand. Arch. Physiol.*, **68**, 232 (1934); *Chem. Abs.*, **28**, 4085 (1934).

[204] Slotta, K. H., Ruschig, H., and Fels, E., *Ber.*, **67B**, 1270 (1934); Fernholz, E , *Ibid.*, 1855; Butenandt, A., and Schmidt, J., *Ibid.*, 2088; von Euler, H., and Brandt, K., *Arkiv Kemi, Mineral Geol.*, **11B**, 51 (1935); *Naturwiss.*, **23**, 544 (1935); Chevallier, A., Cornil, L., and Verdollin, J., *Bull. Acad. Med.*, **114**, 171 (1935); *Chem. Abs.*, **29**, 8088 (1935). Bugyi, B., *Z. ges. exptl. Med.*, **101**, 14 (1937).

[205] Das, N., and Guha, B. C., *Indian J. Med. Research*, **21**, 765 (1934); *Chem. Abs.*, **29**, 1150 (1935).

[206] Allen, E., and Ellis, M. M., *J. Am. Med. Assoc.*, **85**, 94 (1925).

[207] British P. 295,361, Aug. 8, 1927, to Schering-Kahlbaum Co.; *Brit. Chem Abs.*, **B**, 37 (1930).

[208] Lieben, F., and Kraus, H., *Biochem Z.*, **236**, 182 (1931).

[209] Westra, J. J., and Hunter, V , *Proc. Soc. Exp. Biol. Med* , **30**, 1157 (1933); *Chem. Abs.*, **28**, 814 (1934).

[210] Ågren, G., *Skand. Arch. Physiol.*, **70**, 10 (1934); *Chem. Abs.*, **29**, 1475 (1935).

[211] Ludany, G., *Biochem. Z.*, **285**, 192 (1936).

Irradiation of an alkaline extract of the pigment hormone of the posterior lobe of the hypophysis does not affect its ability to cause on injection a temperature decrease and a blood sugar increase.[212]

PRODUCTS OF PATHOLOGICAL SIGNIFICANCE

The toxin, ricin, could not be destroyed by ultraviolet light of wave-lengths 2250 to 2540A in experiments by Carmichael.[213]

Irradiation of tetanus toxin destroys its toxic but not its antigenic powers.[214] The toxicity of diphtheria toxin is also destroyed.[215] Irradiation for 48 hours causes a marked change in the absorption curve.[216]

Tuberculin. High dilutions of tuberculin are markedly inactivated by intense exposures to the quartz lamp.[217] The inactivity of light of short wave-lengths on concentrated "old tuberculin" was considered to be due to the lack of penetration of these rays. In weaker solutions, the activity on intracutaneous injection is diminished but the general reacting power is retained. The therapeutic use of light-treated tuberculin is recommended therefore as obviating the painful cutaneous reactions. This preparation is called ultratuberculin.

After irradiation, the "old tuberculin" solutions were incapable of causing intracutaneous reactions in tuberculosis guinea pigs and in suitable doses did not kill tuberculous guinea pigs.[218] This is in distinction to the results obtained in man, where rayed tuberculin produced both focal and general reactions. This difference is explained by assuming either that unchanged tuberculin is still present after irradiation or that the reactions in man are of a non-specific nature.

During irradiation of tuberculin, the pH of the solutions shifted toward the acid side and the surface tension increased, according to Mikhailovski.[219] Spiegel-Adolf and Seibert [220] measured the ultraviolet absorption spectra of highly purified tuberculin preparations made from various organisms. Considerable variations in absorption were observed. All preparations made from human type bacilli by precipitation with trichloroacetic acid contained a substance showing selective absorption with a maximum at 2650 to 2670A, spectrographically identical with nucleic acid. Nevertheless, the content of nucleic acid as measured by the absorption band could not be correlated with the biological activity of the preparations, since some in which the absorption band was missing were still biologically active. When preparations in 0.1-per cent and 1-per cent concentrations were irradiated in a quartz-covered dish for six to ten hours at 15 cm. from a quartz mercury arc, the absorption band disappeared and the toxicity, as measured by the intradermal test and the lethal action on tuberculous guinea pigs, was lost. Thus, although nucleic acid does not appear to be identical with the potent principle of tuberculin, there seems nevertheless some sort of association between it and the potent principle.

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[212] Jores, A., *Z. ges. exptl. Med.*, **97**, 207 (1935).

[213] Carmichael, E. B., *J. Pharmacol. Exp. Therap.*, **35**, 193 (1929).

[214] Megrail, E., and Welch, H., *Proc. Soc. Biol. Med.*, **28**, 494 (1931).

[215] Nakayama, Y., *Japan. J. Mikrobiol. Path.*, **27**, 990 (1933); *Chem. Abs.*, **27**, 4581 (1933); Lowenstein, *Vienna Z. Path. Therap.*, **15**, 279 (1914); *Chem. Abs.*, **9**, 653 (1915).

[216] Levaditi, C., Loiseau, G., Paic, M., Philippe, M., and Haber, P., *Compt. rend. soc. biol.*, **116**, 609 (1934); *Chem. Abs.*, **28**, 5846 (1934). For further absorption data, see Ottensooser, F., Krupski, A., and Almasy, F., *Biochem. Z.*, **277**, 314 (1935) and Wadsworth, A., Crowe, M. O'L., and Smith, L. A., *Brit. J. Exptl. Path.*, **16**, 201 (1935). From the absorption data, the presence of a hemochromogen is indicated.

[217] Hausmann, W., Neumann, W., and Schuberth, K., *Z. Tuberk.*, **46**, 32 (1926); *Chem. Abs.*, **21**, 3678 (1927); *Z. Tuberk.*, **47**, 113 (1927); *Chem. Abs.*, **22**, 985 (1928).

[218] Fischer, A., and Hausmann, W., *Z. Tuberk.*, **58**, 328 (1930); *Chem. Abs.*, **26**, 511 (1932).

[219] Mikhailovski, S. M., *Zhur. Exp. Biol. Med.*, **9**, 12 (1928); *Chem. Abs.*, **22**, 2760 (1928).

[220] Spiegel-Adolf, M., and Seibert, F. B., *J. Biol. Chem.*, **106**, 373 (1934).

The action of cobra venom on red blood cells is completely destroyed by irradiating it in a dilution of 1 to 2000 in quartz with 72 times an erythema dose of the radiations from a mercury arc at a distance of half a meter.[221] At the same time the toxicity of the venom toward white mice was destroyed or greatly reduced. The possibility of using such attenuated venom in prophylactic treatments is suggested.

Arthus and Collins [222] found also that the toxins of *Crotalus terrificus, Lachesis lanceolatus, Vipera Russellii,* and *Naja tripudians* are decomposed by ultraviolet irradiation. The ability of cobra venom to inhibit coagulation was sometimes so changed as to cause a slight acceleration of coagulation. Snake venom could be protected from the effects of irradiation by egg-white, horse serum or Witte's peptone. Anticobra, antidaboia and antibothrops sera were little affected by irradiation unless diluted. Arthus [223] later stated that in the presence of gelatin, the effect of the treatment was to destroy both the toxicity and the antigenic power of cobra venom. Macht and Davis [224] also found ultraviolet rays to produce a rapid decrease in the potency of snake venom.

Serum "kallicrein" bound by gland activator is destroyed by ultraviolet light, the rate being largely independent of the pH.[225]

The flocculation characteristics of diphtheria toxoid are not changed after two to three hours of exposure to unfiltered mercury arc radiations, but the flocculating ability of the toxins decreased gradually. Their toxicity decreased about 30 per cent. The antiserums lost their flocculating power and not more than 30 per cent of their antitoxic power, although their behavior as regards precipitation by sodium sulfate was not affected.[226]

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[221] Much, Peemöller and Haim, *Münch. Med. Wochschr.*, **74**, 1365; *Chem Abs.*, **22**, 4641 (1928).

[222] Arthus, M., and Collins, H., *Arch. Intern. Physiol.*, **30**, 250 (1928); *Chem. Abs.*, **24**, 2172 (1930); *Brit. Chem. Abs.*, **A**, 1024 (1929).

[223] Arthus, M., *Compt. rend. soc. biol.*, **103**, 130 (1930); *Chem. Abs.*, **25**, 135 (1931).

[224] Macht, D. I., and Davis, M. E., *Proc. Soc. Exptl. Biol. Med.*, **30**, 990 (1933); note also Fulchignoni, E., *Boll. soc. ital. biol. sper.*, **11**, 429 (1936); Kopaczewski, W., *Compt. rend. soc. biol.*, **80**, 884 (1917).

[225] Werle, E., *Biochem. Z.*, **287**, 235 (1936); *Chem. Abs.*, **31**, 149 (1931).

[226] Modern, F., *Rev. inst. bacteriol. dept. nacl. hig. (Buenos Aires)*, **7**, 618 (1936); *Chem. Abs.*, **31**, 2622 (1931).

Chapter 35

The Lethal Action of Ultraviolet Rays and Sterilization

It has been known for over a half a century that ultraviolet rays are capable of killing bacteria and molds, but it is only in comparatively recent times that attempts have been made to utilize these results for the practical sterilization of foods, drugs, water and air. The method has, however, definite limitations and at present its use is becoming more and more restricted to surface sterilization of foods, the treatment of relatively expensive materials such as certain pharmaceutical preparations and the irradiation of air in operating rooms and hospital corridors. Studies of the mechanism of the lethal action are important in that they offer a method of attack on some unsolved problems of physiology and pathology.

EARLY HISTORY

As early as 1877, Downes and Blunt[1] discovered the bactericidal action of light on a mixture of organisms encountered in putrefying substances. They showed that rays of short wave-lengths are responsible for the lethal effects, and that these rays are capable of sterilizing either moist or dry organisms. They ascribed the action to a direct effect upon the organisms rather than to effects upon the surrounding media. They were in error, however, in concluding that the presence of oxygen is essential for bactericidal action. This error persisted a long time, being repeated and emphasized by Roux in 1887,[2] until it was corrected by Ward in 1892.[3] Studies were made of the effect of irradiation upon a number of microörganisms by Arloing[4] and by Duclaux (1885). Ward showed that, although some bactericidal action is exerted by the visible spectrum upon the anthrax bacillus, the most intense lethal effects are due to the ultraviolet rays which fail to penetrate glass. Ward suggested that the carbon arc might be used for the disinfection of small enclosed spaces, such as railway cars.

Other workers added a number of features of physical interest. Such features as the applicability of the inverse square law for the falling off of the intensity of the source with respect to distance, the comparative efficacy of intermittent and continuous irradiation, the effects of temperature and the like, attracted the attention of many workers, particularly of Henri and his collaborators. The general outcome of this work was the realization that physical or photochemical changes were involved which were in some manner dependent upon the absorption of the effective radiations by the organisms.

Ambitious attempts to replace the rather qualitative generalizations of their predecessors by a more quantitative statement of data were made by Bie and Bang in Finsen's laboratory. Each of these observers measured and recorded the energies to which the organisms were subjected in their experiments. Although their work was largely confined to the visible spectrum, it indicated that the bactericidal effect increases sharply as the wave-lengths employed are decreased. Only by the use of long exposures was any germicidal effect obtained by the use of light of the middle range of the visible spectrum. The most valuable contribution of Bie was the introduction of the use of liquid absorption filters to isolate particular spectral regions.

Bang improved the technique by eliminating the heating infrared rays, and extended the measurements into the ultraviolet by the use of quartz. A hanging drop of the bacterial suspension on the lower surface of a quartz plate was exposed to radiations passing through the quartz. The plate formed the lid of a small quartz chamber, the temperature of which was maintained constant by a thermostatically controlled water jacket. Some of the observations indicated not only that the killing may be very rapid when ultraviolet light is employed, but also that the age of the organism and the temperature at which the irradiation is conducted exert an influence on the results. For example, at 30°C., a culture of *B. prodigiosus* three hours old was killed in 60 seconds, but a culture ten to fifteen hours old required 210 seconds. At 45°C., a three-hour culture was killed in fifteen seconds. This indicated that the reaction underlying the lethal mechanism possesses a positive temperature coefficient.[5]

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[1] Downes, A., and Blunt, T. P., *Proc. Roy. Soc.*, **26**, 488 (1877).

[2] Roux, E., *Ann. Inst. Pasteur*, **1**, 445 (1887).

[3] Ward, H. M., *Proc. Roy. Soc.*, **52**, 393 (1893); **53**, 23 (1893); **54**, 472 (1893).

[4] Arloing, S., *Compt. rend.*, **100**, 378 (1885); **101**, 511 (1886).

Bang[6] also presented a curve for the relative effectiveness of various wave-lengths, consideration of which is reserved for a later section.

In 1903, Bernard and Morgan, working in MacFayden's laboratory at the Lister Institute, made a series of experiments which indicated that[7] the bactericidal action is practically confined to the region between 3290 and 2265A. By means of a quartz spectrograph, the spectrum of a carbon arc was thrown upon an agar plate superficially inoculated with a culture of *B. coli communis*. After a definite time the plate was incubated. Only that part of the surface which had been exposed to the rays from 3287 to 2265A showed any sign of bactericidal action. Later workers refining on the technique have fixed these limits somewhat differently. Bernard and Morgan found also that the cadmium and the iron arcs were more efficient than the carbon arc

The active rays were completely arrested by thin films of agar media. The reader is reminded that an agar medium is not a simple gel of agar agar, but contains added proteins and sometimes sugar. These added foodstuffs exert a considerable filtering action. Similar results with a thin membrane of human epidermis stretched as a filter showed that it could not be hoped to sterilize pathogenic organisms located beneath the surface of the skin.

BACTERICIDAL SPECTRAL REGIONS ACCORDING TO EARLIER OBSERVERS

The majority of workers have found the region of bactericidal activity to lie between the wave-lengths 2960 and 2100A. Thus Newcomber,[8] working with the bacillus of typhoid fever, gives the effective limits as 2800 to 2100A with no action at 2970A. Browning and Russ, using agar[9] surface cultures, a tungsten lamp, and a quartz spectrometer, reported 2960 to 2900A as bactericidal rays, with a maximum action at 2800 to 2540A. Cernovodeanu and Henri,[10] using a Cooper-Hewitt lamp and bacterial emulsions, found a maximum at about 2800A; Mashimo,[11] using agar surface cultures and a quartz spectrometer, found the bactericidal range to be from 2950 to 1860A with a maximum at 2750A. Bayne-Jones and von der Lingen[12] give 3500 to 1856A. Bang,[13] using a carbon arc at 30 amperes, found the maximum action to be produced by the wave-length 2500A.

The differences reported may be caused by variations in technique, especially the following: surface cultures can be killed by rays of less penetration, that is, of longer wave-length, than are needed for emulsions. This effect is reversed when the emulsion is agitated during irradiation. Arcs between different electrodes vary in their spectral energy distributions. Temperature and hydrogen ion concentration may affect the results.

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[5] See also Thiele, H., and Wolf, K., *Arch. Hyg.*, **60**, 29; *Chem. Abs.*, **1**, 1029, (1907). Contra: Cernovodeanu, P., and Henri, V., *Compt. rend.*, **150**, 52, 549 (1910)

[6] Bang, S., *Mitteilungen aus Finsen's Medisins Lysinstitut*, **9**, 164 (1905).

[7] Bernard, J. E., and Morgan, H., *Brit. Med. J.*, *Nov.* 14, 1903, *Proc. Roy. Soc.*, **72**, 126 (1903).

[8] Newcomber, H. S., *J. Exp. Med.*, **26**, 841 (1917).

[9] Browning, C. H., and Russ, S., *Proc. Roy. Soc.*, **110**, 33 (1917).

[10] Cernovodeanu, P., and Henri, V., *Compt. rend.*, **150**, 52 (1910).

[11] Mashimo, T., *Mem. Coll. Sci. Kyoto*, **4**, 1 (1919); *J. Sci.*, 161A (1921); *Chem. Abs.*, **15**, 1146 (1921).

[12] Bayne-Jones, S., and von der Lingen, J. S., *Bull. Johns Hopkins Hosp.*, **34**, 11 (1923); *cf.* Bovie, W. T., *Bot. Gaz.*, **61**, 1 (1916).

[13] Bang, S., cited by Henri, V., *Compt. rend.*, **155**, 315 (1912).

On the other hand Bazzoni[14] reported that the full radiation from light source emitting wave-lengths shorter than 2500A will kill bacteria, but that isolate radiations between the limits of 2500 and 2800A will not affect bacteria in a dro of water in an exposure of an hour. He states further that several hours' exposur is needed to kill bacteria with rays of wave-lengths between 2200 and 2250A eve when their intensity is the same as that of the rapidly destructive total radiatio of the same source. These findings are in contradiction with those of many subsequent workers who found bactericidal action even in narrow bands sharply isolate by a quartz spectrometer.

Since little was known regarding the distribution of intensities in the lines c the tungsten arc employed by Browning and Russ, Burger[15] repeated the experiment, using a mercury arc as the light source, and was able to demonstrate som correlation between the intensities of the lines within the lethal region and thei relative killing effects.

In order to determine the practicability of exposing fruit to ultraviolet rays i order to destroy mold spores, Coblentz and Fulton at the Bureau of Standards conducted an investigation of the effects of various wave-length regions upon culture of *Staphylococcus aureus*. In commenting upon the culture spectrogram of Brown and Russ (see Figure 132), they stated that the sharp termination of the germicida action in the short wave-length region may have been due to absorption of thes rays in the instrument employed.

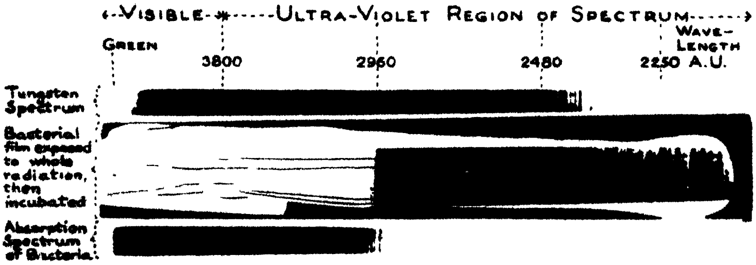
←VISIBLE→←ULTRA-VIOLET REGION OF SPECTRUM→
GREEN
3800
2960
2480
2250 A.U.
WAVE-LENGTH
Tungsten Spectrum
Bacterial film exposed to whole radiation, then incubated
Absorption Spectrum of Bacteria

FIGURE 132. Plate of Bacteria Exposed by Spectrograph by Browning and Russ.

Coblentz and Fulton were unable to detect any effect on growth produced b irradiating agar before seeding it with the cultures, unless very high light intensities were used. The absorption spectrum of the bacterial emulsion extended fron 2960 to 2100A and coincided with the spectral range of germicidal action. Sligh differences in the wave-lengths effective for killing different organisms were found Thus for *B. coli*, the range for lethal effects extended from 2960 to 2200A an for *B. typhosus* from 3000 to 2100A, and for *Staphylococcus aureus* the range o greatest germicidal action extended from 2960 to 2380A. It may be noted that i the experiments of Baynes-Jones and van der Lingen in which the long wave length threshold was found at 3500A, the cultures were exposed to the sun fo three hours. Coblentz and Fulton employed a series of mica screens of variou thicknesses for isolating particular regions, the mica having a maximum absorptio near 2600A. They found germicidal action even at 3650A, but very prolonge exposures were required when wave-lengths between 2970 and 3650A were used

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[14] Bazzoni, C. B., *Am. J. Public Health*, 4, 975 (1914).
[15] Burger, G., *Bull. Basic Sci. Research*, 2, 46 (1928).

The lethal action of rays shorter than 2800A was at least ten times more rapid than that of those longer than 3050A, in spite of the much lower intensity of the shorter rays. Intermittent exposure had the same effect as continuous exposure for the same total time of exposure, that is, the action is cumulative. These authors estimated the energy between 1700 and 2800A required to kill a single bacterium to be of the order of 19×10^{-12} watt.[16]

INTERPRETATIONS OF THE LETHAL MECHANISM

Bedford[17] attempted to revive an earlier theory of an indirect lethal mechanism in which it was assumed that the organisms are killed by the action of hydrogen peroxide formed by the ultraviolet rays. Such a mechanism would require a wave-length dependence similar to that for the production of hydrogen peroxide, which differs from the results described in the preceding paragraphs. Furthermore, such a mechanism is inadequate to account for the observed facts (described in a subsequent paragraph) regarding the relative efficiencies of various wave-lengths operating at the same intensity. Moore and Webster[18] attributed the germicidal power of sunlight to the production of formaldehyde.

Proks[19] claimed that irradiation of the culture medium previous to inoculation lessens its ability to support growth. It may be recalled that Coblentz and Fulton had observed a similar result after prolonged irradiation of agar. Blank and Arnold[20] state that radiations of 2537A change agar or agar-water gels so that they no longer support the growth of *B. subtilis.* There is formed a nonvolatile, thermostable material capable of diffusing through the gel. A similar inhibiting effect results from the addition to the medium of an irradiated solution of a carbohydrate. In confirming these results, Baumgartner[21] notes that irradiation of carbohydrates is accompanied by a marked production of acid, approximately half of which is formic. Neutralization restores the ability of the medium to support growth. Further confirmation is reported by Pratt.[22] Calabek[23] believed that the Höhensonne lamp, as well as natural solar rays, lowers the swelling capacity of agar disks to an extent dependent upon the time of irradiation. The maximum decrease was achieved after an illumination of 146 minutes on one side of the disk, the subsequent swelling in water reaching only 1525 per cent instead of the normal 3200 per cent. The action of the radiations was practically limited to the extreme layers of the gel, decreasing to about zero at 0.08 mm. below the surface. Kersten and Dwight[24] find that irradiation of dry agar decreases the viscosity and pH of the sol subsequently made.

Such effects on the medium have, however, little to do with the mechanism by which organisms on the surface of a plate are killed within a few seconds of exposure to ultraviolet rays. In this case, it is necessary to seek for a direct action of the rays upon the organisms. To determine which of the chemical constituents of the organisms absorb the light in the primary process, subsequent workers have compared the absorption spectra of various cellular components with the spectral regions of greatest lethal activity.[25]

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[16] Coblentz, W. W., and Fulton, H. R., *Bureau of Standards Sci. Papers,* **19,** 495, 641 (1924).

[17] Bedford, T. H., *Brit. J. Exptl. Path.,* **8,** 437 (1927).

[18] Moore, B., and Webster, T. A., *Proc. Roy. Soc.,* **90,** 168 (1918).

[19] Proks, J., *Lait,* **13,** 331 (1933); *Chem. Abs.,* **27,** 3233 (1933). To eliminate effects on the media, D. G. Sharp atomizes broth cultures into air where they may be irradiated. *J. Bact.,* **35,** 589 (1938).

[20] Blank, I. H., and Arnold, W., *J. Bact.,* **30,** 507 (1935).

[21] Baumgartner, J. G., *J. Bact.,* **32,** 75 (1936).

[22] Pratt, E. L., *J. Bact.,* **32,** 613 (1936).

[23] Calabek, J., *Protoplasma,* **3,** 17 (1927); *Chem. Abs.,* **22,** 3896 (1928).

[24] Kersten, H. J., and Dwight, C. H., *J. Phys. Chem.,* **41,** 687 (1937).

Following a suggestion of Henri[26] that the abiotic power of various wave-lengths parallels their absorption by proteins, Harris and Hoyt[27] found that *B. subtilis*, irradiated by ultraviolet filtered through a 1-per cent tyrosine solution, survived exposures of forty minutes. On direct exposure, the organisms were killed in 150 seconds. Similar results were obtained with *Staphylococcus aureus* and *B. mucosus capsulatus.* These experiments do not, however, afford proof that the lethal action of ultraviolet rays is to be attributed to an effect upon the aromatic amino- acids of the proteins. This work had a considerable influence on the opinions of biologists and for a time the effects of radiations upon the proteins were perhaps overemphasized.

In 1914, Henri stated[28] that the abiotic power of ultraviolet light was the result of photochemical action on certain molecular groupings of the protoplasm and, especially, the cell nucleus. In 1916, Galeotti[29] showed that the reproductivity of *B. typhosus*, *B. paratyphosis* and *B. subtilis* could be destroyed by less intense ultraviolet light without causing them to lose their motility, an indication that the first locus of attack is upon some material associated with cell division. Bovie and Hughes[30] found that exposures of *Paramecium caudatum* only one-thirteenth as long as those necessary to produce cytolysis were sufficient to inhibit all division.

Some observers have described changes wrought in bacteria by non-sterilizing doses of ultraviolet rays. Henri[31] claimed to have produced two new forms from anthrax bacilli in this manner. Eberson[32] believed the irradiation of certain types of mengingoccoci to diminish their virulence and increase their antigenic power. However, attention has not been devoted to any extent to this type of ultraviolet effect.

In 1928, Gates published a brief note stating that[33] "the reciprocal of the bactericidal energy curves matches the absorption curves for certain of the nucleoproteins—cytosine, thymine and uracil—more closely than it does those for various aromatic acids such as tyrosine, tryptophane and phenylalanine, suggested by Harris and Hoyt." That derivatives of the nucleic acids should be concerned agrees well with the observations that it is the reproductive function which is first destroyed by the action of ultraviolet rays. It must be remembered that in most experimental work the criterion of death based upon the counting of colonies which grow in media inoculated by irradiated organisms is really a criterion of the failure of cell division to occur at the normal rate.

Gates[34] employed a quartz monochromator to separate the wave-lengths emitted by a quartz mercury arc, and measured the intensity at the exit slit by means of thermopiles. A suspension of *Staphylococcus aureus* was flowed over an agar plate and exposed at the exit slit. After the exposure, this was covered with another layer of agar and incubated. The area counted coincided with the area of the thermopile junction. The energies applied were varied by altering the times of exposure. From a large number of experiments, smooth curves were obtained for the variation in the per cents of bacteria killed with variation in the logarithms of the available energies expressed in ergs per square millimeter.[35] The curves were so similar as to indicate that the reaction at any one wave-length is typical of them all. The form of the S-shaped curves is one frequently encountered in experimental biology. Four conclusions were drawn from this work.

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[25] Rahn, O., [*J. Gen. Physiol.*, **13**, 179, 395; **14**, 315] has assumed that each cell contains one or several extremely sensitive molecules, the destruction or inactivation of any one of these preventing the multiplication of the cell. He believes that it may be necessary for more than one molecule to be destroyed in order that a yeast cell may be killed. In the case of the spores of the mold *Botrytis cinerea,* the number of reacting molecules is thought to be greater than one; and in the flagellate *Colpidium.* Rahn believes that two molecules must be destroyed before mobility ceases.

[26] Henri, V., *Compt. rend. soc. biol.*, **73**, 323.

[27] Harris, F. I., and Hoyt, H. S., *Pathology*, **2**, 245 (1919); *Chem. Abs*, **13**, 2384 (1919).

[28] Henri, Mme., *Compt. rend.*, **158**, 1032 (1914).

[29] Galeotti, G., *Ann. Inst. Pasteur*, **30**, 49 (1916); *Chem. Abs.*, **10**, 2358 (1916).

[30] Bovie, W. T., and Hughes, D. M., *J. Med. Research*, **23**, 223 (1918).

[31] Henri, Mme., *Electrical Review*, **74**, 768 (1914).

[32] Eberson, F., *J. Immunol.*, **5**, 345 (1920); *Chem. Abs.*, **14**, 3273 (1920).

[33] Gates, F. L., *Science*, **58**, 479 (1928).

[34] Gates, F. L., *J. Gen. Physiol.*, **13**, 231 (1929).

1. No bacteria succumb in the initial period of exposure. The energy incident during this initial period is between 6 and 7 per cent of that required to kill all of the organisms.
2. After this period, between 20 and 30 per cent of the organisms were found to be destroyed by less energy than would be predicted from the rate of destruction of the remainder of the organisms. They seem to be less resistant than the rest.
3. A considerable proportion of the remaining bacteria (about 70 or 80 per cent of the total number) succumb along an energy gradient that bears an exponential relationship to the lethal effect, *i.e.*, a straight line. In other words, the middle portion of the curve may be reproduced by the equation describing the course of a monomolecular reaction.
4. In the final period there are remaining a number of organisms which are killed only by an excess of energy.

The second feature discussed above is attributed to the fact that young bacteria are less resistant than are older, resting organisms, a fact which had been demonstrated by Bang.[36] Gates was of the opinion that there was no evidence in his work that sublethal doses exerted any stimulating effect on the subsequent multiplication of bacteria, although this had been claimed by Browning and Russ.[37] This may have been due to the fact that when few bacteria survive in the middle of an exposed area, or when relatively few are left at the edges where the intensity of the radiation falls away, the colonies they produce are always much larger than those in the more crowded areas of the plate. The reason for the more active multiplication and consequent large colonies under these circumstances Gates believed to be merely that the nutrient substances per colony are not so limited, and also that waste products do not accumulate so rapidly.

One point of view regarding the nature of the lethal process disregards the features indicative of individual differences in the resistance of the organisms and considers the curve evidence for a fundamental monomolecular reaction underlying the process. Another point of view, to which Gates inclined, regards the course as determined by probability considerations and suggests that it should be compared with the mortality curves of insurance statistics. The similarity of the middle portion of the curve to that of monomolecular reactions is ascribed to a coincidence in the distribution of the resistance factors.

Gates showed[38] that wide variations in the intensities of incident ultraviolet energy (from 21.6 to 5.6 ergs per sq. mm.) were not accurately compensated for by making the appropriate changes in the times of irradiation. Thus the Bunsen-

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[35] Hertel, E., [*Z. allgem. Physiol.*, **4**, 1 (1904); **5**, 95 (1905)] had made a beginning in this type of work, but he had reported only on the effects of six lines. Compare also Bang, S., *loc. cit.*

[36] Bang, S., *Mitteilungen aus Finsen's Lichtinstitut*, **2**, 1 (1901).

[37] Browning, C. H., and Russ, S., *Proc. Roy. Soc.*, **110**, 33 (1917).

[38] Gates, F. L., *J. Gen. Physiol.*, **13**, 249 (1929).

Roscoe reciprocity law does not hold strictly. The deviations were most marked with young organisms, metabolically and genetically active.

An exposure of thirty minutes at 3340 or 3660A failed to reduce the subsequent formation of colonies. Although the first experiments with 3130A indicated some bactericidal action, in later ones in which stray reflected light was more rigorously excluded, even very large incident energies had no appreciable effect.

No attempt was made to determine the short wave-length limits of lethal action. Weak lines at 2340, 2300 and 2250A required such long exposures that it was possible to establish only the middle portion of the curve of lethal action. Lyman[39] showed the bactericidal effects of radiations shorter than 1860A and Bovie[40] extended the lower limit to 1250A by the use of a hydrogen discharge tube and fluorite windows.

The lethal action has a temperature coefficient of 1.1, in agreement with the observations of Baynes-Jones and van der Lingen. Gates was unable to confirm the results of Thiele and Wolf,[41] and of Wiesner[42] who found an increase in temperature to extend the bactericidal zone toward the longer wave-lengths.

Variations in the pH of the medium between 4.5 and 7.5 were without influence on the lethal action, but at pH 9 and 10 there was a slight but definite increase in bacterial sensitivity. Plane-polarization of the incident ultraviolet light had no effect upon bactericidal action.[43]

Although the killing curves obtained by the use of different wave-lengths are similar in form, they lie at very different energy levels.[44] Thus energy required to kill half of the exposed organisms ranges from 3150 ergs per sq. mm. at 3020A to only 88 at 2660A. The latter wave-length has been reported to be optimum for killing organisms, longer or shorter ones requiring more incident energy. On plotting against the wave-lengths as abscissae the reciprocals of the energies required at various wave-lengths to kill half of the organisms, the curves showed a maximum at 2660A, a minimum near 2400A and another maximum beyond 2300A. A similar curve was obtained for *B. coli*.[45] Absorption curves of thin films of the organisms pressed between quartz plates were strikingly similar to the curves for the reciprocals of the energies required.

Comparatively few references are available on the absorption of the materials of the cell nucleus. Dhéré in 1906 stated that 4-methyluracil exhibits an absorption band between 2346 and 2801A. Since this was very similar to the absorption observed in the case of nucleic acid, he attributed the absorption spectrum of the latter to its pyrimidine and purine components. Holiday[46] more recently reported quantitative data on the absorption spectra of several purines.

Heyroth and Loofbourow[47] gave absorption curves for a number of purines and pyrimidines and showed that the absorption of thymonucleic acid may be represented as the summation of the molar extinction coefficients, at least at 2600A of

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[39] Lyman, T., "Spectroscopy of the Extreme Ultraviolet," Longmans, Green and Company, pp. 1-3, 2nd ed., London, 1928.

[40] Bovie, W. T., *Bot. Gaz.*, **61**, 1 (1916).

[41] Thiele, H., and Wolf, K., *Arch. Hyg.*, **60**, 29, *Chem. Abs.*, **1**, 1029 (1907).

[42] Wiesner, R., *Arch. Hyg.*, **61**, 1 (1907).

[43] Bhatnagar, S. S., and Lal, R. B., [*Nature*, **117**, 302 (1926)] had previously suggested as a result of preliminary experiments on *B. typhosus* and *Vibrio cholerae* that bacterial life is favorably affected by polarized light as compared with ordinary light of equal intensity.

[44] Gates, F. L., *J. Gen. Physiol.*, **14**, 31 (1930). *Cf.*, however, Herčik, F., *J. Gen. Physiol.*, **20**, 589 (1937).

[45] For *E. coli*, V. Henri finds the maximum bactericidal action at 2750A. *Festschr. Zangger*, **2**, 792 (1935); *Ber. ges. Physiol. exptl. Pharmakol.*, **86**, 363; *Chem. Abs.*, **31**, 6683 (1937).

[46] Holiday, E. R., *Biochem. J.*, **24**, 619 (1930).

[47] Heyroth, F. F., and Loofbourow, J. R., *J. Am. Chem. Soc.*, **53**, 3441 (1931); **56**, 1728 (1934).

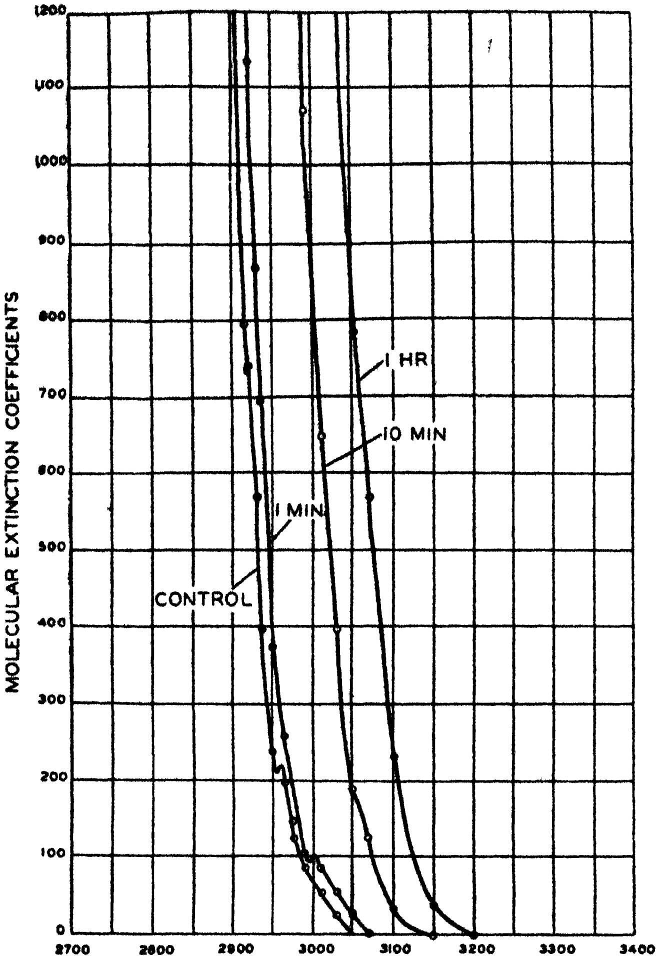

FIGURE 133. Absorption of Uracil at one gram per liter, Showing Effect of Irradiation with Full Ultraviolet (Heyroth and Loofbourow, *Journal American Chemical Society*).

adenine, guanine, cytosine and thymine. They advanced arguments for viewing their absorption data as supporting the hypothesis of Gates that it is energy absorbed by these cellular components which is concerned in the lethal mechanism.[48] The absorption of the typical pyrimidine, uracil, in a concentration roughly comparable to that estimated as present in the cell nucleus, rises very abruptly and rapidly at about 2950A. This is the wave-length found by many workers to represent the approximate lethal threshold for the rapid action of ultraviolet rays on bacteria. (See Figure 133.) The concentration of one gm. per liter was chosen for these measurements because of the following considerations. Assuming for tubercle bacilli a water content of 70 per cent and in the dried material a fat content of 40 per cent, the work of Johnson and Brown, who obtained 7.7 gms. of a nucleic acid from 436 gms. of dried and fat-free bacteria, would indicate the presence of at least 0.3 per cent of this nucleic acid in the fresh organisms.[49] Assuming for this tuberculinic acid a molecular weight approximately that of thymonucleic acid, the absorbing nitrogenous bases would be at least one two-hundredth per cent of the weight of the fresh bacteria. A solution of one gm. per liter of any one of the absorbing bases would be of the same order of concentration as in the fresh bacteria.

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[48] Heyroth, F. F., and Loofbourow, J. R., *Bull. Basic Sci. Research*, 5, 13 (1933).

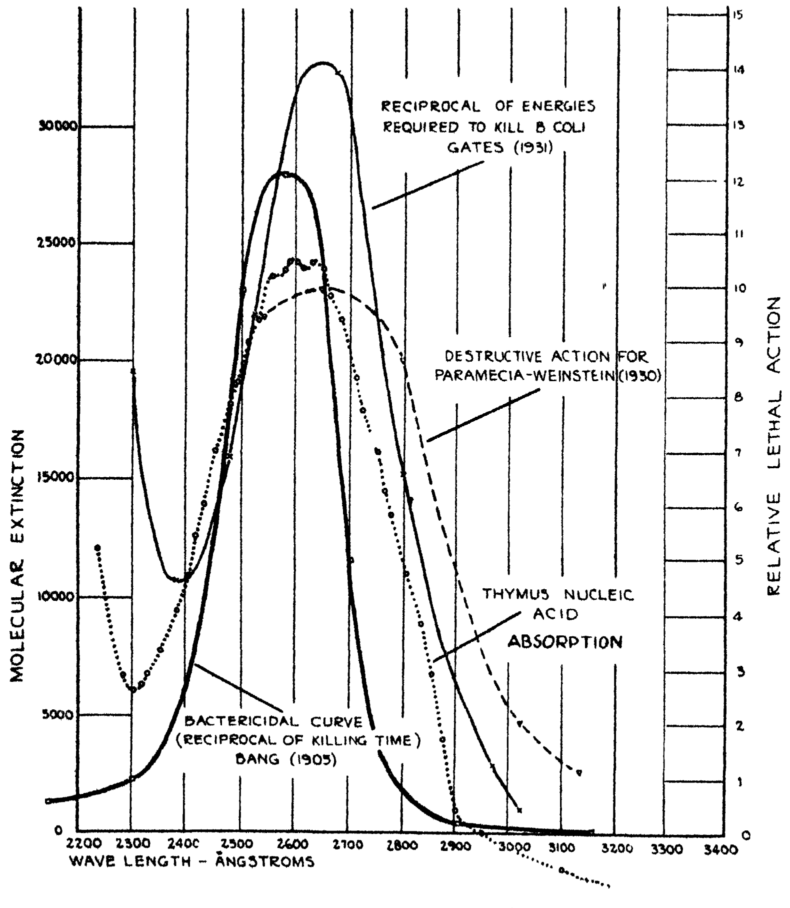

FIGURE 134. Comparison of Lethal Action of Ultraviolet and Absorption of Nuclear Materials. (Heyroth and Loofbourow, *Bull. Basic Sci. Research.*)

It is apparent that the absorption curve of these pyrimidine and purine bases in concentrations comparable to those found in the cell corresponds closely to the lethal threshold for the killing of microörganisms. As indicated by the figure, this long-wave absorption curve for high concentrations of the nuclear materials moves toward still longer wave-lengths during the irradiation of these substances with unfiltered ultraviolet light. This produces a filtering effect which tends to screen the unchanged substances from the destructive action of the radiations. It is a matter of extreme interest that this occurs particularly with respect to the shortest wave-lengths that may be found in the solar spectrum as available on the surface of the earth.

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[49] Johnson, T. B., and Brown, E. B., *J. Biol. Chem.*, 54, 721 (1922).

The point of maximum absorption by most of these pyrimidine and purine bases and by nucleic acid itself lies near 2600A.[50] To make clear the similarity between the forms of these absorption curves and those of the reciprocals of the energies required for killing, and interpreted by Gates as the curve for the absorption by the sensitive materials in the cells, curves have been plotted in Figure 134. These compare the data of Gates, of Bang and of Weinstein (for the killing of Paramecia) with the [51] absorption curve of nucleic acid. Both the nucleic acids from yeast and from thymus glands have the same type of absorption curve.

Only in those organisms in which the nuclear material is diffused throughout the cell (bacteria and yeasts) or in which the nucleus is unprotected by a thick layer of cytoplasm should the absorption by nucleic acid be expected to play a predominant role in the lethal action. Proteins may play a more important role in the effects on cells such as the protozoa in which the nucleus is more adequately protected by a thicker surrounding layer of protoplasm. The thickness of such a cytoplasmic layer in many of the protozoa may exceed many times the entire diameter of bacteria. Indeed, in the case of such large cells there is some evidence to show that the optimum lethal action takes place rather closer to 2800A, the position of the absorption maximum of the proteins, than to 2600A, the position of the maximum absorption by nucleic acid. A quantitative comparison of the absorption of equally concentrated protein and nucleic acid solutions shows that a far greater proportion of the incident energy is absorbed at their respective maxima by the nucleic acid than by the proteins. The absorption of the proteins in this region is due (see the preceding chapter), to the tyrosine, tryptophane and other aromatic amino- acid components. Not only are the molecular extinction coefficients of tyrosine (approximately 2000 cm.$^{-1}$), and of tryptophane (5000 cm.$^{-1}$) at 2800A lower than those found at 2600A for adenine (10,300 cm.$^{-1}$), guanine (12,000 cm.$^{-1}$), cytosine (6100 cm.$^{-1}$), thymine (9000 cm.$^{-1}$) and uracil (9100 cm.$^{-1}$), but their proportions in the molecules of proteins (rarely over 2 per cent) are much less than those of the absorbing nitrogen ring compounds in the molecules of nucleic acids.

Relatively little is yet known as to the nature of the changes induced in the pyrimidines by the action of ultraviolet rays. The absorption spectrum changes during irradiation in the manner indicated in Fig. 135.[52] The molecular extinction curve of uracil is given in the upper heavy curve (concentration of 10 mg. per liter). During the first few minutes of irradiation with full ultraviolet light from a mercury arc there is a definite rise in absorption in the region from 2200 to 2300A and also in the region of wave-lengths longer than 2900A. During the later periods of irradiation, the absorption of the head of the band decreases. In the case of uracil this change occurs after fifteen minutes of exposure at 2 cm. from a Victor water-cooled arc. For a time the rise in absorption at both legs of the curve continues although the absorption at the center of the band is diminishing. After about fifteen minutes, however, the absorption between 2200 and 2300A also begins to decrease, although that of the rays of wave-length longer than 2900A continues to increase for three hours and then decreases. If the radiation is sufficiently prolonged, practically all selective absorption is lost, the absorbed energy causing photochemical changes which destroy the pyrimidines. In the case of nucleic acid, an irradiation of an hour caused but negligible change between 2500 to 2900A, but in the region near 2300A the extinction coefficients increased nearly 45 per cent. The position of the minimum shifted slightly toward longer wave-lengths during this period. On more prolonged irradiation the absorption at the head of the band decreased.

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[50] Heyroth, F. F., and Loofbourow, J. R., *J. Am. Chem. Soc.*, **53**, 3441 (1931).

[51] Weinstein, I., *J Opt. Soc. Am.*, **20**, 433 (1930).

[52] Heyroth, F. F., and Loofbourow, J. R., *J. Am. Chem. Soc.*, **53**, 3441 (1931).

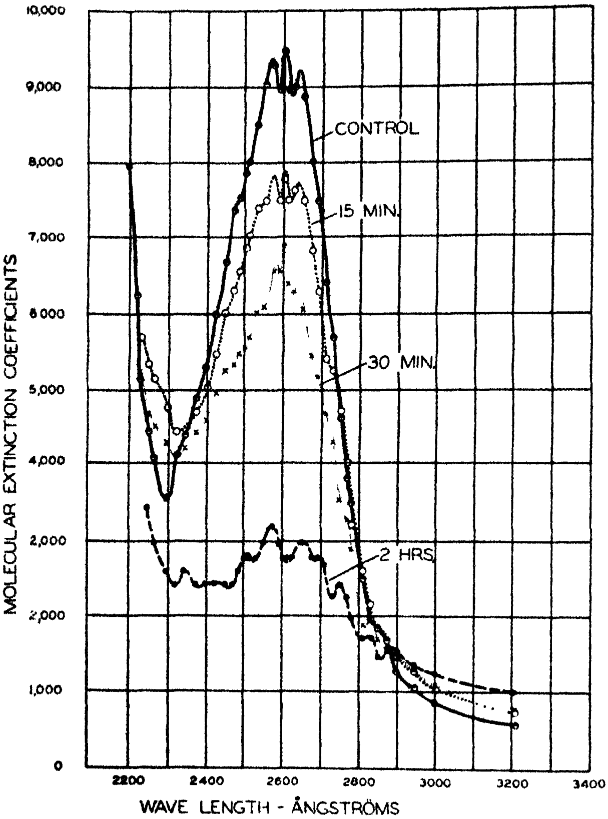

FIGURE 135. Effect of Ultraviolet Irradiation upon the Absorption Spectrum of Uracil. (Heyroth and Loofbourow, *Journal American Chemical Society.*)

The mechanism underlying these changes is as yet unknown. There may be either a rupture of the ring with the production of diactinic products of the nature of urea and open-chain three-carbon compounds, or there may be a gradual saturation of the ring. Bass has shown that thymine, after twelve hours of ultraviolet irradiation in the presence of oxygen and ferrous salts, yields urea and pyruvic acid.[53] Lieben and Getreuer,[54] state that no ammonia is liberated during the irradiation of uric acid, xanthine, uracil, alloxan, hydantoin and α-hydroxynicotinic acid. There is, however, evidence of an increase in free amino- groups indicative of a rupture of the ring. Sodium nucleate is relatively resistant to rupture. Histidine, proline, guanine, pyridine and nicotinic acid evolve ammonia. In these cases the destructive effect apparently is hastened by oxygenation, but the latter is not essential to the change.

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[53] Bass, L. W., *J. Am. Chem. Soc.*, 46, 190 (1924).

[54] Lieben, F., and Getreuer. V., *Biochem Z.*, 259, 1 (1933).

It was suggested by Heyroth and Loofbourow that the early change might involve the formation of a compound of the type of α-isouracil described by Tafel and Houseman.[55] Since the formula proposed by those workers involved the presence of a hydroxyl group in position five, and since Johnson and Johns[56] had concluded that the ability of pyrimidine compounds to reduce phosphotungstic acid in alkaline solution depends on the presence of amino- or hydroxyl groups in this position, Heyroth[57] investigated the effect of irradiation upon the ability of uracil to reduce this reagent. It was found that irradiation of a uracil solution induces a photochemical change resulting in the formation of a substance or substances capable of reducing an arsenophosphotungstic acid solution. The rate of change was greatest early in the irradiation. The observation of the occurrence of this reaction may be of aid in the interpretation of certain findings in the physiology of irradiation. Clinical observations of an 80-per cent increase in the blood uric acid and purines have been reported by Wiener[58] to occur in patients undergoing phototherapy. Koch and Reed[59] reported a 38-per cent increase in the blood uric acid of a dog during irradiation with a carbon arc for an hour and a half. The blood was irradiated while flowing through quartz tubes introduced into the circulation. These authors did not attribute the increased values to the formation of uric acid but instead to the presence of some substance giving a similar reduction of the uric acid reagent (phosphotungstic acid) used for the determination of the so-called blood uric acid. Dillman[60] could not obtain the increase when the blood was irradiated *in vitro*. He also noted that irradiation of uric acid destroys its ability to reduce phosphotungstic acid. The observations on uracil suggest the purine or pyrimidine nucleosides of the blood as a possible source from which such a reducing substance might be formed during irradiation. Pincussen and Flores[61] by experiments *in vitro* attempted to learn something of the fate of nucleins exposed to radiations. Specimens of nucleic acid were exposed to the rays of a Nitra lamp, the heat rays being removed by a water filter. Eosin and dichloroanthracene were tested as sensitizing agents, and the changes in the specific rotation of the solution of nucleic acid were followed. A splitting of the acid was pronounced without sensitizer or in the presence of eosin, but was not detected in the presence of the anthracene compound. The nucleic acid-splitting enzymes did not appear to be increased when animals were irradiated.

Ultraviolet photomicrographs of the chromosomes of *Drosophila* in various fluid reagents have been given by Hellström, Brandt and von Euler.[62]

Peptization of cell colloids was obtained when a sharp pencil of ultraviolet light was passed into the macronuclei of *Paramecium caudatum*, *Spirostomum ambiguum*, and *Amphileptus claparedei*.[63] Microscopic ultraviolet absorption methods have been employed to follow the distribution of nucleic acid in tissues during the proc-

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[55] Tafel, J., and Houseman, P. A., *Ber.*, 40, 3743 (1907).

[56] Johnson, T. B., and Johns, C. O., *J. Am. Chem. Soc.*, 36, 970 (1914).

[57] Heyroth, F. F., *Bull. Basic Sci. Research*, 4, 128 (1932).

[58] Wiener, H., *Klin. Wochschr.*, 3, 936 (1924).

[59] Koch, F. C., and Reed, C. I., *Am. J. Physiol.*, 75, 351 (1925)

[60] Dillman, L. M., *J. Lab. Clin. Med*, 17, 44 (1931).

[61] Pincussen, L., and Flores, A., *Biochem. Z.*, 126, 86 (1921). See also Chapter 33.

[62] Hellström, H., Brandt, K., and von Euler, H., *Svensk Kem. Tids.*, 47, 249 (1935); *Mikrochemie, Festschr. Hans Molisch*, 2093 (1936).

esses of mitosis and glandular secretion.[64] In the large chromosomes of *Stenobothrus* spermatocytes, the absorption curves correspond to those of a 15-per cent solution of thymonucleic acid. Chromosomes are built up of alternating nucleic acid segments and protein segments.[65]

Interesting observations of another type relating to the effect of ultraviolet rays in killing *Escherishia coli* have been reported by Lisse and Tittsler.[66] By the use of either Northrop-Kunitz or Falk capillary electrophoresis cells, they found that irradiation, if of sufficient duration, produces a decrease in the negative charge of the organism. With the former type of cell they found some indication of an initial stimulative action of the ultraviolet radiations which made itself felt in an increase of the negative charge. This could not, however, be observed with the Falk capillary cell. Short irradiations which merely stimulate or injure the cells permit a return of the electrokinetic velocity toward its normal value, but prolonged lethal irradiation produces a lasting effect. The sequence of decreasing electrophoretic velocities is the same as that of increasing susceptibility to agglutination except in the case of very long or very short irradiations. The interposition of a Corex A filter causes a practical disappearance of this sequence of agglutinability. Irradiation by a carbon arc also produced lysis which was the greater the longer the irradiation. Irradiation produced an increase in the pH of an aqueous suspension of cells, the original pH of which was approximately 6.1. With 500-watt Mazda bulbs as the light source there was eventually a reduction of the charge and evidence of lysis indicated by a clearing of the suspension, but much longer times of irradiation were required than when ultraviolet light was used. Norton [67] also suggested that the changes suffered by bacteria on exposure to ultraviolet rays may be accompanied or perhaps preceded by changes in the electrical charges borne by the bacteria.[68]

Gärtner [69] finds the agglutinability of bacterial suspensions to be increased and the zone of acid agglutination widened by irradiation, although the acid zone is narrowed by prolonged exposures. Basic dyes agglutinate irradiated bacteria in lower concentrations. The pH is increased and the acid-binding power decreased. Agglutinability with antiserum is decreased.

Pincussen and Gutfeld [70] studied the influence of salt solutions on the killing of various organisms by light. With *Staphylococcus aureus*, the killing effect in calcium chloride solutions was about three times that obtained in distilled water, but other salts, including the chlorides of sodium, potassium and magnesium, were without this influence. Calcium chloride had a protective action on the diphtheria bacillus, the action of light being about four times greater in distilled water. Ehrismann [71] studied the effect of various cations in inhibiting the lysis or clearing of suspensions of bacteria. The process is recognized by a decrease in the volume

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[63] Tchakhotine, S., *Compt. rend.*, **202**, 778 (1936).

[64] Casperson, T., *Skand. Arch. Physiol. Suppl.*, **8**, 151 pp (1936): *Bull. histol appl. physiol. path tech. microscop.*, **14**, 33 (1937): *Protoplasma*, **27**, 463 (1937); Casperson, T., Hammarsten, E., and Hammarsten, H., *Trans. Faraday Soc.*, **31**, 367 (1935).

[65] Casperson, T., *Naturwiss.*, **23**, 527 (1935).

[66] Lisse, M. W., and Tittsler, R. P., *Proc Soc. Exp. Biol. Med.*, **28**, 811 (1931).

[67] Norton, J. F., in Jordan, E. O., and Falk, J. S., "Newer Knowledge of Bacteriology and Epidemiology," Univ. of Chicago Press, 374 (1928).

[68] For other references to this work, see Lisse, M. W., *Penn. Agr. Sta Tech. Bull.*, **230**, 6 (1928), **243**, 6 (1929); **258**, 8 (1930); Tittsler, R. P., and Dozois, K. P., *Ibid.*, **258**, 28 (1930); Lisse, M. W., Tittsler, R. P., and Sharpless, G. R., *Ibid.*, **276**, 4 (1932). The last includes an exhaustive bibliography on the lethal action of ultraviolet rays.

[69] Gärtner, I., *Z. Immunitäts*, **80**, 493 (1933); *Chem. Abs.*, **28**, 5491 (1934); Gärtner, I., and Szathmary, J., *Z. Immunitäts*, **78**, 249 (1933).

[70] Pincussen, L., and Gutfeld, F. V., *Centr. Bakt. Parasitenk., 1 Abt.*, 109 (1928).

[71] Ehrismann, O., *Z. Hyg. Infektionskrankh.*, **111**, 618 (1930); *Chem. Abs.*, **25**, 721 (1931).

of the suspended particles or by the appearance of nitrogenous compounds in the surrounding fluid. An accelerated decomposition of the bacterial proteins into amino- acids could not, however, be demonstrated. The following cations inhibit the action in the order indicated: $La^{++} > Ca^{++} > Ba^{++} > Sr^{++} > Mg^{++} > Na^{+}$ or Li^{+} or K^{+}. Also an increase in temperature, displacement of the pH to the acid side, the addition of formaldehyde or of mercuric chloride inhibit decomposition. The various bacteria studied could be arranged in a series according to their sensitiveness.

Number of Quanta Per Bacterium Required for Killing. The question has been raised as to the number of quanta which must hit a single organism, which of course is itself a system containing many molecules, in order to kill it. The reasoning involved has been discussed by Wyckoff for killing bacteria by high-velocity electrons,[72] where it appeared that the absorption of a single high-voltage electron by a colon bacillus was sufficient to cause death.

In the case of the killing by x-rays,[73] Wyckoff found that the absorption of a single x-ray quantum of energy sufficed to kill an organism, although only about one in twenty of the absorbed quanta was effective. From this he concluded that within the organism there is some sensitive region the destruction of which leads to death, and that this sensitive "cell" must have a volume less than 6 per cent of the bacterium itself.

The case is somewhat different in the lethal action of ultraviolet rays. Wyckoff [74] interpreted the results of Gates on *Staphylococcus aureus* as indicating curves of a "multiple-hit-to-kill" type. Since he believed that the tendency of this organism to cling together in chains made it impossible to spread them properly, he repeated the experiments with the more motile *B. coli.* Survival-ratio curves at various wave-lengths when plotted on semilogarithmic paper gave straight lines, indicating an exponential killing rate. This might be due either to a single quantum-hit killing the organism or to a suitable distribution of the sensitivities of the bacteria. The slope of these curves at all wave-lengths less than 3000A indicated an average number of effective absorptions per bacterium per second of somewhat less than 0.03. From the intensity of the energy and the volume of the bacterium, it could be calculated that for the 2699A line, the radiant energy absorbed per bacterium per second was 0.99×10^{6} erg. Since each quantum at this wave-length represents 7.25×10^{-12} erg, the total number of quanta absorbed per bacterium per second was calculated to be 136,000. But of these, less than one (0.03) was effective in causing death. Thus only 0.03/136,000 or one in 4.19×10^{6} of the absorbed quanta was effective. Wyckoff then proceeded to multiply the volume of one bacterium (3.93×10^{-13} cc.) by a fraction 0.03/136,000 and thus obtained what he considered to be a sensitive volume, which was 9.38×10^{-20} cc. As it could be calculated that this is approximately the volume which might be occupied by an average-sized protein molecule, it was possible to make the suggestion, although with reservations, that the lethal action depends upon an effect upon one protein molecule in the organism. That the explanation was unlikely was indicated by the fact that the millions of non-lethal quanta absorbed per bacterium did not cause any alteration in the growth rate. However this may be, the data indicate for the organism a very low quantum yield. In liquid or solid systems low quantum yields do not necessarily imply the existence of some unusually sensitive substrate molecule or unit cell. Other explanations of the low quantum yield will undoubtedly be advanced when the photochemical reactions leading to the death of the organism are better understood.

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[72] Wyckoff, R. W. G., *J. Exp. Med.*, **51**, 921 (1930).

[73] Wyckoff, R. W. G., *J. Exp. Med.*, **52**, 435, 769 (1930).

[74] Wyckoff, R. W. G., *J. Gen. Physiol.*, **15**, 351 (1932).

In general, Wyckoff found the energies required to kill half of the organisms at various wave-lengths to be of the same order as those reported by Gates. Like Gates, he found that the greatest effectiveness lies at about 2652A. There are, however, some discrepancies between the energies found by Gates and by Wyckoff, for which no explanation is yet apparent. It is also interesting to note that Wyckoff found at 3132A that the curve for survival-ratios against time could not be indicated on semilogarithmic paper by a straight line with the same accuracy as the curves obtained at other wave-lengths. It seems possible that the mechanism of killing at wave-lengths longer than 2900A is different from that at the shorter wave-lengths.

Evidence for a variation in the resistance of individual cells has occasionally been noted, particularly in the work of Gates previously discussed. Beauverie [75] finds that the resistance of yeast cells increases in proportion to their glycogen content.

Although all microscopic living forms can be killed by ultraviolet light, they exhibit varying degrees of resistance either inherent and specific to the organism, or extrinsic and due to the conditions of the irradiation. Among themselves bacteria show considerable, and to some extent characteristic, variations of resistance from species to species. But an attempt to employ these variations for the differentiation of bacteria was unsuccessful.[76] Nogemi [77] finds that *Es. coli*, streptococci and the cholera vibrio are killed readily and that the tubercle and anthrax bacilli are more resistant. In general spores are somewhat more resistant than vegetative forms.[78]

Sunlight has a deleterious action on cultures of *Brucella abortus*, sterilizing them in three hours. Ultraviolet light has a similar effect.[79]

According to Mayer and Dworski,[80] a suspension of tubercle bacilli containing 2,750,000 organisms per cc. was killed within four minutes by the absorption of 1.42×10^9 ergs per sq. cm. from unfiltered radiations of the quartz mercury arc. Exposure to an intensity of 5.93×10^6 ergs per sq. cm. per second for 25 minutes did not alter the acid-fast staining qualities of these organisms. When fixed by heat and irradiated for 5 to 25 minutes, the bacilli showed changes indicative of disintegration, since irregularities were observed on staining by the Ziehl-Neelsen method.

Akiyama [81] claims that *Es. coli*, *Sal. typhimurium* and staphylococci in salt solution are more resistant to ultraviolet light when sensitized with their own specific serums than when treated with heterologous immune serums or with normal serum. The bacteria treated with the globulin fraction of the specific immune serums are more resistant than those treated with the albumin fractions of the same serums.

Bacteria killed by ultraviolet light lose a considerable part of their toxicity toward laboratory test animals, but completely retain their antigenic and immunizing characteristics.[82]

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[75] Beauverie, J., *Compt. rend.*, 199, 81 (1934).

[76] Browning, C. H., and Russ, S., "Applied Physiology," p. 150, Oxford University Press, 1918.

[77] Nogemi, Y., *Kitasato Arch. Exp. Med.*, 10, 135 (1933).

[78] Lagerberg, O., *Z. Immunitäts.*, 28, 186 (1919); *Chem. Abs.*, 13, 2385 (1919).

[79] Morales-Otero, P., *Puerto Rico J. Pub. Health & Trop. Med.*, 6, 1 (1930).

[80] Mayer, E., and Dworski, M., *Tubercle*, 13, 500 (1932).

[81] Akiyama, M., *Sei-ikai Med. J.*, 54, No. 5, 840 (1935); *Chem. Abs.*, 30, 3018 (1936).

[82] Trotskii, V. L., Sviridova, T. A., and Super, L. P., *J. Microbiol., Epidemiol., Immunobiol.*, 15, 519 (1935); *Chem. Abs.*, 30, 4531 (1936).

Recently, Hollaender and Claus [83] have given data on the energy required for the inactivation of *Es. coli* as a function of the wave-lengths employed. At 2250A, the ergs required per bacterium were 41.3×10^{-6}; at 2650A, 13.1×10^{-6}; and at 2950A, 81.6×10^{-6}. These values were regarded as somewhat more accurate than those cited in preceding paragraphs since they were calculated by a method which corrected for the protective action of nonviable organisms.

Lehner [84] states that although *Rhodovibrio* is killed quickly by ultraviolet rays, *Thiocystis* is not killed by an exposure of an hour, and that short exposures accelerate growth.

ACTION OF ULTRAVIOLET RAYS ON YEAST

Lacasagne [85] exposed *Saccharomyces ellipsoideus* to radiations of wave-lengths between 2800 and 3800A and found the cells to fall into three classes according to their susceptibility to the rays. Some died immediately, some after a certain period and others exhibited only a retarded rate of cell division but ultimately recovered their power of reproduction. Wyckoff and Luyet [86] made similar observations and noted the production of some giant cells. Their results tended to indicate "multiple-quantum-hit" relations.

In the work of Oster [87] carefully prepared suspensions of *Saccharomyces cerevisae* containing practically no clumps of cells were employed. Following irradiation, observation with a microscope revealed certain abnormalities in cell growth and reproduction. There was apparent a period of survival during which normal colonies could not be formed, after irradiation by each of the wave-lengths (2225 to 3132A) studied. There could be distinguished single cells of normal size and not visibly altered, single cells of giant size, two-cell groups usually from three to eight times the size of normal two-cell groups and more spherical in shape and often showing a long filament-like process constricted at intervals along the length, three to eight-cell groups of giants, which at this stage either cease budding or go on to furnish buds of normal size, and finally larger groups which, although retarded in their ability to form normal-sized colonies show little evidence of giantism. At all wave-lengths, a definite, measurable retardation in reproduction as based upon the criterion of culture formation could be demonstrated. The size of the colonies increased at a rate roughly proportional to the increase in incident energy. The relation between the percentage of inhibition and the incident energy appeared to be logarithmic over the inhibitory range. When the period of exposure was increased beyond this point, various degrees of injury occurred and finally all budding and growth could be stopped. As a criterion of lethal action, Oster adopted the inability of the yeast cell to form two or more daughter cells rather than merely the inhibition of macroscopic colonies. The survival-ratio is then the ratio of the number of cells which bud at least twice to the original number of exposed cells. For each of several wave-lengths shorter than 2900A curves were plotted of the survival-ratio against the energy in ergs per sq. mm. In the case of longer wave-lengths very much more incident energy was required for lethal effects.

The curves revealed that for all wave-lengths studied the energy which had to be applied before any of the cells were killed was approximately 8 per cent of that required

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[83] Hollaender, A., and Claus, W. D., *J. Gen. Physiol.*, **19**, 753 (1936).

[84] Lehner, A., *Zentr. Bakt., Parasitenk., (Abt. II)*, **97**, 65 (1937); *Chem. Abs.*, **32**, 1743 (1938).

[85] Lacasagne, A., *Compt. rend.*, **190**, 524 (1930).

[86] Wyckoff, W. R. G., and Luyet, B. J., *Radiology*, **17**, 1171 (1931).

[87] Oster, R. H., *J. Gen. Physiol.*, **18**, 71 (1934-5).

> to kill all the cells. Between 20 and 30 per cent of the cells do not survive after an exposure relatively short in comparison with that required to suppress budding in all of the cells. The remaining 70 or 80 per cent require from 70 to 80 per cent of the energy required to kill all the cells. The last 2 or 3 per cent of the cells are affected at a slightly lower rate. Cells irradiated with small amounts of energy show a much lower rate of budding with a longer initial lag period than that of the typical growth curve of normal cells. The age of the cells has a marked influence upon their resistance, from 20 to 50 per cent more energy being required to produce a given effect on a fifteen-day culture than on 24-hour cultures. In the former, a greater proportion of the cells is in the resting stage.[88]
>
> The temperature coefficient is low, about 1.06 to 1.1, in agreement with that obtained by Gates on bacteria. The irradiation effects are exerted directly upon the organisms since irradiation of the malt-agar medium for periods from five minutes to two hours had no effect upon the growth of organisms subsequently planted in it. For intensity variations up to 30 per cent, the rate of absorption of photons by the cells did not markedly affect the lethal action.
>
> Attempts to determine the absorption spectrum of yeast failed to give satisfactory results. However, an application of the method of Gates of plotting the reciprocals of the energies required to cause death in 50 per cent of the cells against the wave-lengths employed, gave results similar to those reported by Gates for bacteria. The necessary energies ranged from 457 ergs per sq. mm. at 2652A to 23,500 ergs at 3022A, or roughly five times the energy range for *Staphylococcus aureus.*

From the individual survival-ratio curves plotted against the incident energies applied, Oster calculated (by a method devised by Curie,[89] which differs somewhat from that employed by Wyckoff), the number of quantum-hits necessary to kill at various wave-lengths. The results indicated a "multiple-quantum hit-to-kill" relation, the minimum number of quantum hits varying from about four to about six. The shape of the curves was believed to suggest that other factors than single quantum hits on several molecules are involved, as suggested by Rahn, or multiple-quantum hits on a sensitive volume element, as suggested by Wyckoff and Luyet.

Stimulation of Yeast There have been many attempts to show the stimulation of yeast growth by irradiation by ultraviolet light. Some authors believed that wave-lengths somewhat longer than the lethal ones have such an action. Loofbourow and Cameron, who reviewed the literature,[90] were themselves unable to detect such an action, and this is the generally accepted conclusion.

There have, however, been suggestions that sublethal doses of radiation in the lethal wave-length range may produce injuries of the cells by virtue of which products capable of stimulating the growth of other cells are formed. Hollaender and Duggar [91] observed that cells from the 10 per cent which survived a certain irradiation in isotonic salt suspension by the 2650A rays increased in number when transferred to salt solutions (single or balanced) in which normal control cells died. Fardon, Norris, Loofbourow and Ruddy [92] claimed that substances which stimulate the respiration of other cells are produced in cells injured by ultraviolet light. Subsequently, these observers [93] devised a method for demonstrating the formation of growth-stimulating substances in the injured cells. The active substances were allowed to diffuse from the injured cells through an agar gel upon the surface of which a fresh colony was placed. Colonies grew more rapidly on agar above injured cells than on agar above normal cells.

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[88] For comparison with the effects of x-rays at various stages of the reproductive period, see Lacasagne, A., and Holweck, F., *Compt. rend soc biol*, **104**, 1221 (1930); *Compt. rend.*, **190**, 524, 527 (1930); *Compt. rend. soc. biol.*, **103**, 60 (1930); Strangeways, T. S. P., and Hopwood, F. L., *Proc. Roy. Soc.*, **100B**, 283 (1926); Holweck, F, *Congress Intern. Elec., Paris*, **10**, 1 (1932).

[89] Curie, M., *Compt. rend.*, **188**, 202 (1929).

[90] Loofbourow, J. R., and Cameron, J., *Bull. Basic Sci. Research*, **5**, 33 (1933).

[91] Hollaender, A., and Duggar, B. M., *J. Bact.*, **33**, 16 (1937).

[92] Fardon, J., Norris, R. J., Loofbourow, J. R., and Ruddy, M., *Nature*, **139**, 589 (1937); Fardon, J. C., Carroll, M. J., and Veronita, M., *Studies Inst. Divi Thomae*, **1**, 17, 41 (1937).

[93] Sperti, G., Loofbourow, J. R., and Dwyer, C. M., *Studies Inst. Divi Thomae*, **1**, 162 (1937).

In earlier experiments, Pulkki[94] had been unable to produce a stimulant for *B. mycoides* by irradiation of yeast cells. Abderhalden[95] was unable to alter significantly the course of alcoholic fermentation due to yeast cells by the addition of alcoholic extracts of irradiated yeast, irradiated yeast macerated juice, or ergosterol. Woodrow, Bailey and Fulmer[96] believed irradiation of yeast culture media produces a non-volatile toxic material derived from the sugar present, but Oster was unable to detect any toxic substance liberated by the organism during its irradiation.

Suranyi and Vermes[97] claimed to have observed an increase of about 50 per cent in the oxygen consumption of yeast at pH 7.2 during irradiation. Oster, however, could detect no observable effects on oxygen consumption until more than 80 per cent of the organisms had been so affected that normal colonies did not result from their subsequent growth.

Teindl-Czech[98] found visible light to have no influence on the division rhythm of yeast cells. The same was true for very small exposures from an unfiltered Uviol lamp. Immediately after medium doses the number of cell divisions decreased: this was followed by a temporary rise and a new decrease. During irradiation the yeast appeared slightly vitreous and turbid. With strong doses, abnormal cell forms appeared. Irradiation by the region between 2300 and 4000A in the absence of oxygen may be used to secure yeast cells of uniform potency.[99]

Fermentation. Zeller[100] found sunlight to inhibit the output of carbon dioxide from yeast after a temporary slight stimulation. Guerrini[101] inoculated yeast into 5-per cent glucose solutions and incubated the cultures in darkness, in daylight and in light filtered through red, green, yellow and blue screens. He claimed to find the liberation of carbon dioxide to be greater in cultures exposed to light than in those in darkness. In general, the greatest quantities of carbon dioxide were produced in red light, the next greatest in yellow, then in green and the least in blue light. The last gave practically no carbon dioxide. Murakami[102] found that in the fermentation of koji extract the production of alcohol was maximal under a red light of wave-length longer than 6200A, increasing in general with the wave-length. The maximum yield of aldehyde was obtained under wave-lengths between 3960 and 5400A. Acetal was produced abundantly under a white light. The production of volatile acid was greatest in darkness and that of non-volatile acid greatest in violet to yellow light. The production of esters was generally higher under light of longer wave-lengths. There have been a number of claims that ultraviolet light increases the fermentative power of yeast.

Lindner[103] found that under normal conditions 30 gms. of dextrose gave 119 cc. of carbon dioxide in 24 hours and under ultraviolet irradiation 2743 cc. In the same period.[104] De Fazi[105] claimed to have observed a stimulation of growth and fermentation of yeast. His investigations involved in some cases irradiation of the water used in dissolving the sugar to be fermented rather than of the yeast or fermenting mixture. Even under the former conditions, some stimulation was stated to occur. Also, such claims have been made by Sanzo and Pirrone.[106]

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[94] Pulkki, L. H., *Ann. Acad. Sci. Fennicae,* **A41,** No. 1 (1935); *Chem. Abs.,* **30,** 4898 (1936).

[95] Abderhalden, E., *Fermentforsch.,* **9,** 195 (1927); *Brit. Chem. Abs.,* **A,** 1113 (1927).

[96] Woodrow, J. W., Bailey, A. C., and Fulmer, E. I., *Plant Physiol.,* **2,** 71 (1927).

[97] Suranyi, G., and Vermes, M., *Magyar Orvosi Arch.,* **30,** 585 (1929); *Chem. Abs.,* **25,** 2162 (1931).

[98] Teindl-Czech, L., *Protoplasma,* **27,** 313 (1937). Note also Palmieri, G. G., and Giordano, G., *Boll. soc. ital. biol. sper.,* **7,** 1318 (1932); *Chem. Abs.,* **27,** 1371 (1933).

[99] Light, R. F., Frey, C. N., and Patitz, G. J., U. S. P. 2,099,025, Nov. 16, 1937; *Chem. Abs.,* **32,** 300 (1938).

[100] Zeller, H., *Biochem. Z.,* **171,** 45 (1926).

[101] Guerrini, G., *Boll. soc. ital. biol. sper.,* **5,** 635, 1098 (1930); *Chem Abs.,* **25,** 534 (1931).

[102] Murakami, R., *J. Agr. Chem. Soc. Japan,* **8,** 1237 (1932); **9,** 672 (1933); *Chem. Abs.,* **27,** 1983, 5470 (1933); *Bull. Utsunomiya Agr. Coll.,* **3,** 29 (1933); *Chem. Abs.,* **28,** 3519 (1934).

[103] Lindner, P., *Woch. Brau.,* **39,** 166 (1922); *Chem. Abs.,* **17,** 1686 (1923).

Owen and Mobley[107] have reported that exposure of yeast to ultraviolet light increases its growth and its fermenting power. An exposure of one minute to radiations of wavelengths 2300 to 3100A gave the greatest stimulation, but an exposure of three minutes had the opposite effect. Since a similar stimulation could be brought about, they believed, by the irradiation of sterilized molasses wort, they did not attribute the stimulation to the death of harmful contaminating microörganisms. Beckwith and Donovick[108] exposed a 36-hour culture of purified brewers' yeast in a layer 1.15 cm. thick to ultraviolet radiations for 1.4 seconds per cc. Of the irradiated culture, 125 cc. were added to 1600 cc. of sterilized beer wort and incubated at 28°C. for 32 days. Alcohol formation was at first depressed, but from the 9th to 32nd days exceeded that in the control. Irradiation of the wort alone was without effect. Marmeli and Baratto[109] find that fermentation may be accelerated by addition of small quantities of such substances as ascorbic acid, β-carotene, acamnine, adenine, phytin or inosine. The effects were claimed to be enhanced by previous irradiation of these substances.

Tanner[110] found ultraviolet light to have only a depressing action on fermentation, whether the yeast, the fermenting culture or the glucose broth was the subject of the irradiation. According to Reynolds and Wynd,[111] the inhibition of fermentation by radiations between 3000 and 2500A is a specific effect independent of general injury to the cells. Von Euler and Swartz[112] believed the efficacy of ultraviolet light in accelerating the synthesis of organic phosphoric esters during fermentation to be doubtful, although the inorganic phosphate is decreased.

According to Keeser,[113] glucolysis of 0.1-per cent glucose solution in the presence of yeast cells was accelerated by irradiation with red light for thirty minutes, but white, green or blue light had little effect. Similar results were obtained with fructose, and also in the glucolysis of glucose or fructose by guinea pig serum. Irradiation of ox serum for five hours did not alter the reducing power or content of inorganic phosphorus of the serum, but ultraviolet irradiation increased the reducing power without altering the inorganic phosphorus.

The effect of carbon monoxide in inhibiting the anaerobic fermentation of tetanus or gas gangrene bacilli is increased by light, according to Schlayer.[114] Since only the combination of carbon monoxide with an iron compound is dissociated by light, the fermentation enzyme of these organisms must be an iron catalyst. In the case of an anaerobic butyric acid fermentation process, Kempner and Kubowitz[115] could demonstrate a similar phenomenon only at low temperatures and by the use of very great light intensities. Under these conditions, the fermentation can be completely and reversibly inhibited by carbon monoxide, light destroying the inhibition. The light-sensitivity is very much smaller than in the case of the carbon monoxide combination with the enzyme concerned with respiration. The carbon monoxide compound of the enzyme concerned in the butyric acid fermentation absorbs within the special range 6500 to 3660A.

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[104] See also Söhngen, N. L., and Coolhaas, C., *Woch. Brau*, **40**, 187 (1923); *Chem. Abs.*, **18**, 1030 (1924); Rennhard, A. W., *Compt. rend. soc. biol.*, **89**, 1080 (1923).

[105] De Fazi, R., *Ann. Chim. Applicata*, **4**, 301 (1915); **6**, 221 (1916); **8**, 93 (1917); *Chem. Abs.*, **10**, 950 (1916); *J. Ind. Eng. Chem.*, **13**, 265 (1921); *Atti R Accad. Lincei*, **5**, 344, 901 (1927); *Brit. Chem. Abs.*, **A**, 592, 1113 (1927); *Chem. Abs.*, **21**, 2045 (1927).

[106] Sanzo, L., and Pirrone, F., *Atti Accad. Lincei*, **13**, 613 (1931); *Chem. Abs.*, **26**, 2990 (1932).

[107] Owen, W. L., and Mobley, R. L., *Zentr Bakt. Parasitenk., Abt. II*, **88**, 273 (1933); *Chem. Abs.*, **27**, 5470 (1933); Owen, W. L., *Food Ind.*, **5**, 252 (1933); *Chem. Abs.*, **28**, 254 (1934).

[108] Beckwith, T. D., and Donovick, S. E., *Proc. Soc. Exptl. Biol. Med*, **35**, 36 (1936).

[109] Marmeli, E., and Baratto, A., *Ann. chim. farm.*, No. 1, 18 (1938); *Chem. Abs.*, **32**, 6269 (1938).

[110] Tanner, F. W., *J. Ind. Eng. Chem.*, **13**, 265 (1921); *Chem. Gaz.*, **75**, 309 (1923); Tanner, F. W., and Byerley, J. R., *Arch. Microbiol.*, **5**, 349 (1934); *Chem. Abs.*, **28**, 5594 (1934).

[111] Reynolds, E. S., and Wynd, F. L., *Ann. Mo. Botan. Gardens*, **22**, 853 (1935); *Chem. Abs.*, **30**, 3855 (1936).

[112] von Euler, H., and Swartz, O., *Arkiv Kemi, Mineral. Geol.*, **9**, 21 (1925).

[113] Keeser, E., *Arch. Exptl. Path. Pharmakol.*, **170**, 500 (1933).

[114] Schlayer, C., *Biochem. Z.*, **276**, 460 (1935).

[115] Kempner, W., and Kubowitz, F., *Biochem. Z.*, **265**, 245 (1933).

The action of photocatalysts in the fermentation of lactose by *Es. coli* is stimulating or inhibiting according to the quantity and quality of the catalyst.[116]

Molds. Reports on molds are conflicting. Some workers state that molds are killed by exposure to ultraviolet light without much difficulty.[117] Others report that molds are killed by ordinary exposure only when present in very small amounts. Some molds have protection in the form of fatty or waxy secretions. The latter may shield the mold from some radiations.

Fulton and Coblentz [118] exposed spores of 27 species of fungi for one minute to ultraviolet radiation from a mercury tungsten arc at a distance of six inches. There was complete killing of the spores of 16 species and a survival of less than 1 per cent in four species. It was hoped that this process could be applied to the killing of molds and fungi on oranges. Such a dosage caused no injury to the fruit. The limitation of the method, however, lies in the fact that the rays do not penetrate sufficiently beneath the surface to afford complete disinfection of the fruit.

Dillon-Weston [119] finds the spores of *Puccinia graminis tritici* to be killed more easily when irradiated in water than when irradiated dry. The white and orange specimens of certain physiological forms of the fungus are more susceptible than the red and gray ones. The pigments of the spore walls probably have some protective action. Sibilia [120] believed that ultraviolet rays activate the germination of the teleutospores of *Puccinia coronifera* of oats and *P. triticina* and to a lesser extent of *P. graminis.*

Smith [121] finds the death of *Fusarium* spores exposed to ultraviolet light at different temperatures to take the form of sigmoid curves which rapidly approach the logarithmic type as the temperature is increased. The average temperature coefficient between 0 and 40°C. is 1.13, but between 40 and 50°C. it is 1.37.

Johnson [122] finds rays in the Schumann region to be highly destructive to the upper layers of the mycelium of the fungi, *Collybia dryophila, Sclerotium batacicola,* and *Fusarium batacia.* The effect was localized and did not extend deeply into the culture. Ultraviolet rays passing through Vitaglass had a more injurious effect than those passing the Corning filter 980A. Those passing through Cellophane were intermediate in their action. According to Ramsey and Bailey,[123] irradiation by a quartz mercury arc stimulates spore formation in cultures of *Macrosporium tomato* and *Fusarium cepae.*[124]

Viruses and Bacteriophages. According to Baker and Nanavutty,[125] the bacteriophages are about as susceptible as the bacteria to irradiation, and the relative efficiencies of various spectral regions are about the same as for *B. coli.* Mizuno[126] found the destructive action to vary with the medium, being weak in broth, moderate in water and strongest on agar plates. Among the bacteriophages which have been affected by irradiation are those for *B. coli D,*[127] cholera, staphylococci, and dysentery.[128] The ultraviolet absorption of colon bacteriophages has been measured by Sandholzer, Mann and Berry.[129]

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[116] Guerrini, G., *Boll. soc. ital. biol. sper.*, 10, 847 (1935); *Chem. Abs.*, 30, 8284 (1936).

[117] Houghton, E. M., and Davis, L., *Am. J. Public Health*, 4, 224 (1914); Fairhall, L. T., and Bates, P. M., *The Cotton Oil Press*, 33 (1921).

[118] Fulton, H. R., and Coblentz, W. W., *J. Agr. Research*, 38, 159 (1929).

[119] Dillon-Weston, W. A. R., *Sci. Agr.*, 12, 81 (1931); *Chem. Abs.*, 26, 497 (1932); Dillon-Weston, W. A. R., and Halnan, E. T., *Phytopathology*, 20, 959 (1930); *Chem. Abs.*, 25, 2233 (1931).

[120] Sibilia, C., *Boll. staz. patol. vegetale*, 11, 115 (1931); *Chem. Abs.*, 26, 1958 (1932).

[121] Smith, E., *Bull. Torrey Bot. Club*, 62, 45 (1935); *Chem. Abs.*, 29, 1130 (1935).

[122] Johnson, F. H., *Phytopathology*, 22, 277 (1932).

[123] Ramsey, G. B., and Bailey, A. A., *Bot. Gaz.*, 89, 113 (1930); *Chem. Abs.*, 24, 3261 (1930).

[124] See Hutchinson, A. H., and Ashton, M. R., [*Canadian J. Research*, 3, 187 (1930); *Chem. Abs.*, 25, 315 (1931)] for the action of various mercury lines on the fungus, *Colletotrichum phomoides.*

[125] Baker, S. L., and Nanavutty, S. H., *Brit. J. Exp. Path.*, 10, 45 (1929); see also Appelmans, R., *Arch. Intern. Pharmacodyn.*, 27, 95 (1922); *Chem. Abs.*, 17, 1978 (1923).

The work of Rivers and Gates[130] indicates that the susceptibility of vaccinia virus to irradiation is of the same order as that of bacteria. Galloway[131] finds the virus of foot-and-mouth disease to be destroyed after five minutes of exposure of filtrates to the radiations of a quartz mercury arc in quartz vessels. Also, the virus is inactivated after thirty minutes if the rays are filtered through Vitaglass. In ordinary glass there is no lethal action.

The tobacco mosaic disease virus is similarly inactivated,[132] unless it has penetrated plant tissue. Stanley[133] finds 0.5-per cent solutions of the crystallized protein of this virus to produce (when irradiated for eight hours by the unfiltered rays of a quartz mercury arc) an inactive protein which retains certain chemical and serological properties of the original. However, the protein no longer is capable of producing either the mosaic disease or a high molecular weight protein on inoculation into Turkish tobacco plants. Neither does it cause local lesions in *Nicotinea glutinosa.* The product may be crystallized from solution but the crystal is more opalescent and more readily denatured than before irradiation. Its x-ray diffraction pattern, isoelectric point and optical rotation are unchanged. No marked change in molecular weight occurs, although the homogeneity of the molecules is decreased. The serum of an animal previously injected with the irradiated product has a neutralizing effect on the original virus. The survival-ratios during irradiation follow a simple exponential curve, the rate of the inactivation depending upon the incident energy, according to Price and Gowen.[134] The absorption spectrum of the crystalline virus differs from that of other proteins in having its absorption maximum at 2650A.[135] This suggests that the compound is a nucleoprotein, and for this there is independent chemical evidence. This suggestion is interesting in that it points to the conclusion that viruses, which lie on the border between the living and the lifeless, appear to have nucleic acid as a component.

Other viruses found to be inactivated by ultraviolet rays include those of herpes and encephalitis,[136] influenza,[137] and crystalline tomato bushy stunt virus.[138]

It has been shown by Herzberg[139] that certain dyes can sensitize the vaccine virus to visible light. Only the thiazine, acridine and thioxanthone dyes were stated to have this property. At a dilution of one in a million, methylene blue and thiopyronin acted the most rapidly, sensitizing the virus within twenty to forty seconds. For exposures of an hour the acridine dyes were found to be effective in the greatest dilutions, one in fifty million. It was pointed out that irradiation of rabbit skin by short wave-lengths after the application of active virus (within eight hours of the inoculation) reduced the number of pustules produced, but no effects could be observed if the irradiation was given after sixteen hours. After the injection of methylene blue intravenously, irradiation modified the infection even when given 24 hours after inoculation. With light of longer wavelengths, no modification could be produced by irradiations made later than seven hours after the inoculation, even in the presence of the dye. The same effect was obtained with sunlight used 24 hours after inoculation as with the best source of ultraviolet light used 72 hours after inoculation.

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[126] Mizuno, K., *Japan J. Med. Sci., Bact. & Parasit.,* **1,** 52 (1929); *Chem. Abs.,* **23,** 5485 (1929).

[127] McKinley, E. B., Fisher, R., and Holden, M., *Proc. Soc. Exptl. Biol. Med.,* **23,** 408 (1926).

[128] Levaditi, C., and Voet, J., *Compt. rend. soc. biol.,* **120,** 385 (1935); *Chem. Abs.,* **30,** 1084 (1936); see also Hallauer, C., *Z. Infektionskrankh.,* **117,** 18 (1935).

[129] Sandholzer, L. A., Mann, M., and Berry, G. P., *J. Bact.,* **33,** 17 (1937).

[130] Rivers, T. M., and Gates, F. L., *J. Exp. Med.,* **47,** 45 (1928).

[131] Galloway, I. A., *Brit. J. Exptl. Path.,* **9,** 326 (1928).

[132] Arthur, J. M., and Newell, J. M., *Am. J. Bot.,* **16,** 338 (1929); **15,** 623 (1928).

[133] Stanley, W. M., *Science,* **83,** 626 (1936).

[134] Price, W. C., and Gowen, J. W., *Phytopathology,* **27,** 267 (1937).

[135] Lavin, G. I., and Stanley, W. M., *J. Biol. Chem.,* **118,** 269 (1937).

[136] McKinley, E. B., Fisher, R., and Holden, M., *Proc. Soc. Exptl. Biol. Med.,* **23,** 408 (1926).

[137] Wells, W. F., and Brown, H. W., *Am. J. Hyg.,* **24,** 407 (1936).

[138] Bawden, F. C., and Pirie, N. W., *Brit. J. Exptl. Path.,* **19,** 251 (1938).

[139] Herzberg, K., *Z. Immunitäts,* **80,** 507 (1933); *Chem. Abs.,* **28,** 5126 (1934).

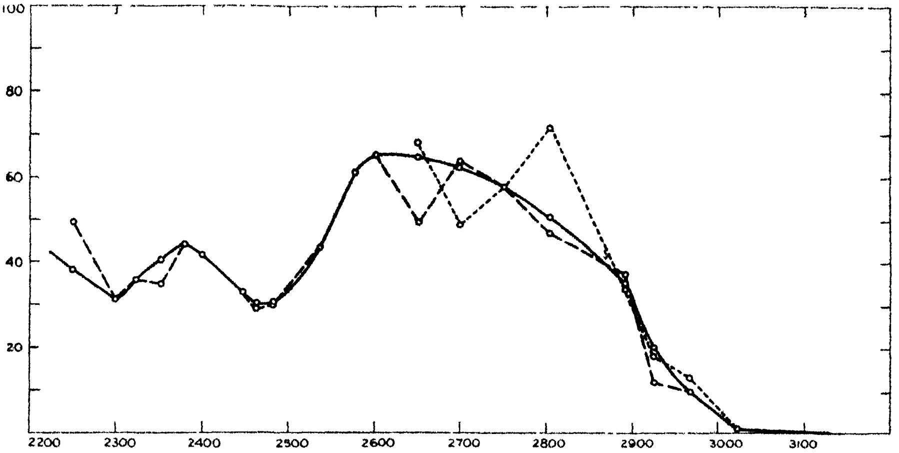

FIGURE 136. Radiotoxic Spectral Sensitivity of *Chlorella vulgaris* to Ultraviolet Rays. (From Meier, Smithsonian Miscellaneous Collections. The abscissae are wavelengths in Angstroms. The ordinates are relative lethal effectiveness in arbitrary units. Black line, smooth curve; dash line, actual values; dotted line, curve obtained by Meier, 1934).

Algae. Lami[140] found that ultraviolet irradiation of the alga, *Bonnemasonia asperagoides,* causes liberation of iodine from the gland cells. In the case of *Euglena,* Swann and del Rosario[141] found that in killing by α-particles, death was caused by a single impact with some sensitive entity of the cell, the size of which was about equal to that of the nucleus. In experiments with ultraviolet light, it appeared that the cells did not cease to die the moment irradiation was stopped, some cells apparently being affected in a manner which produced death some time later. Attempts were made to utilize absorption data on different parts of the cell to compute the volume of an assumed sensitive entity, on the assumption that the probability of reaction following absorption of a photon is unity. Attempts were also made to calculate the probability of killing on the basis that the volume of the assumed sensitive entity is that of the nucleus.

Meier[142] reported that the unicellular green alga, *Chlorella vulgaris,* is not killed by wave-lengths longer than 3022A. In subsequent work,[143] she irradiated agar plates and inoculated them. As normal growth resulted, she concluded that radiations lethal to the organisms did not affect the medium in any way to accelerate or retard growth. She then made a number of exposures of plates (inoculated two to five months previously) behind a spectrograph for various periods from a few seconds to several hours and noted the regions in which decolorized areas became evident at intervals of from a few days to two months following irradiation. The lethal radiotoxic threshold for wave-lengths 2652 and 2804A lies between 100 and 120 seconds for intensities of 1960 and 1840 ergs per sq. cm. per second, respectively. Assuming the Bunsen-Roscoe law, for 1000 ergs per sq. cm. per second, the exposures required for 2652A would be 220 seconds and for 2804A, 206 seconds. Similarly, the results at a number of other wave-lengths were reduced to this common intensity and plotted in Figure 136 which shows a maximum lethal sensitivity at about 2600A. (Note similarity to the observations of Gates on bacteria.)[144] At the suggestion of Dr. C. G. Abbot, she introduced two new terms, radiotoxic spectral sensitivity and radiotoxic virulence. The former related to the certainty of the lethal action and the latter to the quickness of the attack. The distinction was drawn because death ensued much more quickly after irradiation in some spectral regions than in others. The data on the radiotoxic virulence are included in Figure 137 and show an alternate waxing and waning with decreasing wave-length and a high maximum at 2323A.[145]

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[140] Lami, R., *Compt. rend.*, **191,** 863 (1930).

[141] Swann, W. F. G., and del Rosario, C., *J. Franklin Inst.*, **213,** 549 (1932).

[142] Meier, F., *Smithsonian Misc. Coll.*, **87,** No. 10 (1932).

[143] Meier, F., *Ibid.*, **92,** No. 3 (1934); **95,** No. 2 (1936).

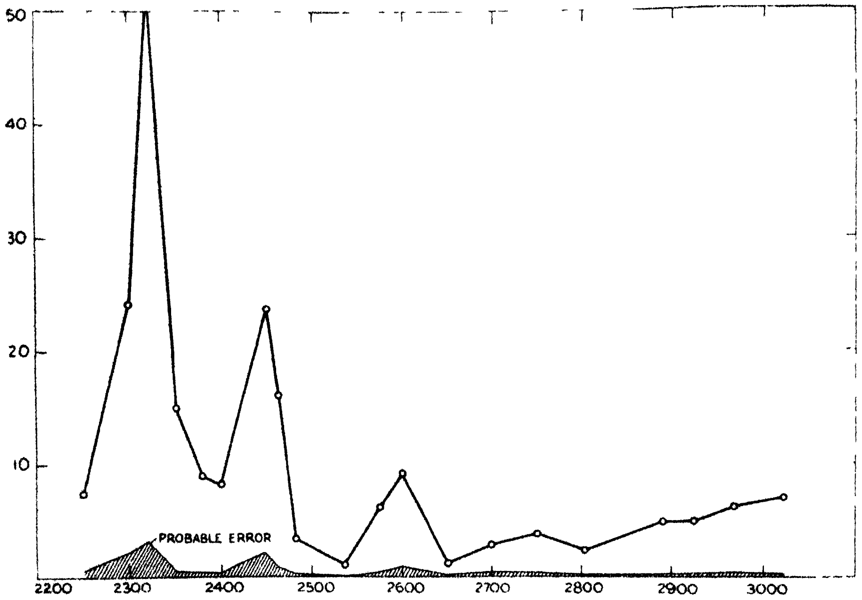

FIGURE 137. Radiotoxic Virulence Determined from *Chlorella vulgaris*. (From Meier, Smithsonian Miscellaneous Collections). The abscissae are wave-lengths in Ångstroms. The ordinates are radiotoxic virulence in arbitrary units.

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[144] Note also Duggar, B. M., and Hollaender, A., *J. Bact.*, **27**, 219 (1934), Lucas, F., *Bell System Tech. Publ. Metallurgy Monogr.*, **B 792**, 1-47.

[145] For effects of portions of the visible and ultraviolet spectrum on cells of the prothallium of ferns, see Charlton, F. B., *Am. J. Botany*, **25**, 431 (1938).

Higher Plants. Hertel examined leaves of the aquatic plant *Elodea canadensis* under a microscope with a quartz condenser and illuminated with light of 2800A. The streaming movement of the granules in the living cells ceased almost immediately.

Work relating to the lethal effects of ultraviolet light on plant cells has been reviewed by Delf.[146] That single exposures may produce severe reactions was demonstrated by Maquenne and Demoussy in 1909, Kluyver in 1911, Ursprung and Blum in 1917, and Stoklasa in 1911. In Kluyver's experiment, exposures at 40 cm. from a mercury-vapor lamp for two and a half hours showed no immediate effects on leaves of *Aucubus*. Subsequently, however, the epidermal cells died, turning black in all leaves which had been exposed for forty minutes or longer. A cover glass protected a leaf from lethal effects over an exposure of twenty hours, indicating that rays of 3000A or longer do not have a directly harmful effect on the plant. The red pigment of *Begonia* was destroyed by illumination for two and a half hours.

According to Ursprung and Blum, in *Pelargonium* the white parts are more resistant to ultraviolet than the green ones in the variegated leaf but in *Vicia faba* the opposite seems to be true. In general, it seems that the guard cells of the stomata are the most resistant of all the epidermal cells. The epidermis, and especially the cuticle, appear to absorb ultraviolet light, the cells being destroyed by the irradiation although the tissues below appear unharmed. Russell and Russell showed that cress seedlings grown on muslin were stunted by mercury-arc irradiation and that those irradiated for periods as long as twenty minutes daily were shriveled in appearance.[147]

Delf, Ritson and Westbrook [148] tested the effects of very short daily exposures to the mercury arc upon a variety of plants. In general, they noted delayed germination, retarded growth and stunted habit of the seedlings and a partial inhibition of leaf development, especially of the lamina. In some cases there was a darker green color and in one case a loss of anthocyanin pigment in the lamina. With longer exposures, older plants showed a promoted leaf fall, and retardation of flower formation and of the opening of previously formed buds. In these cases the exposures were from two to ten minutes repeated from four to eight times daily. With exposures of thirty seconds or less the results were different. In one case, flowering of *Pelargonium* seemed to be promoted, in another the leaves of the irradiated plant ultimately surpassed those of the control in size; and in a third case, after a month of thirty-second daily irradiations at a distance of eight feet, there was a permanent and very favorable after effect in *Trifolium*. In the plant *Voandzeia*, exposures of five minutes daily led to definite anatomical changes during development, such as a reduction in the total thickness of lamina, development of more compact mesophyll with smaller and fewer air spaces, reduction in mechanical tissue and collapse of the cells of the upper epidermis followed by the withdrawal of the chloroplasts from the upper parts of the palisade cells. Martin and Westbrook [149] made histological examinations of leaves (*Pulmonaria* or *Aucuba*) at varying periods during irradiation. Lethal changes were first evident in the epidermal cells in the nuclei which coagulate, darken and become disorganized to one or more irregular masses. Later the cytoplasm becomes finely granular and rapidly darkens. For small doses the reciprocal of the latent period for visible browning is proportional to the dose expressed in Clark lithopone units, but doses between ten and fifteen units make the latent period very short. During irradiation the temperature coefficient was about 1.1, but during the latent period it was higher, from 1.32 to 2.9.

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[146] Delf, E. M., *Brit. J. Actinotherap.*, 2, 106 (1927).

[147] Kluyver, A. J., *Sitzb. Math. Acad. Wiss., Wien.*, 120, 195 (1911); *Chem. Abs.*, 6, 3108 (1912); Ursprung, A., and Blum, G., *Ber. Deut. Bot. Ges.*, 35, 385 (1917); Russell, E. H., and Russell, W. K., "Ultraviolet Radiation and Actinotherapy," New York, Wm. Wood, 1925.

[148] Delf, E. M., Ritson, K., and Westbrook, A., *Brit. J. Exptl. Biol.*, 5, 138 (1927).

[149] Martin, B. T., and Westbrook, M. A., *J. Exptl. Biol.*, 7, 293 (1930).

Gilles,[150] states that the germination of lentil and turnip seeds is accelerated but their growth is somewhat retarded by mercury-arc irradiation.

Protozoa. There have been comparatively few investigations of the effects of ultraviolet light on amoebae.[151] Heilbrunn and Daugherty assumed that ultraviolet rays cause first a breakdown of a calcium gel in the cortex followed by the entry of this calcium into the interior where it produces a preliminary liquefaction followed by gelation. According to Black[152] media which favor motility tend to exert a synergistic action with the rays (2540A) in decreasing motility and producing cytolysis.

Paramecia have been studied under radiations. Hughes and Bovie[153] observed cytolysis in this organism under ultraviolet irradiation. Harris and Hoyt[154] employed paramecia in their work on the significance of the aromatic amino- acids to which allusion has been made. Bovie and Daland[155] found the short rays in the fluorite region to render *Paramecium caudatum* so sensitive to heat that amounts of heat insufficient to affect non-irradiated cells become lethal. Longer exposures to these rays caused death directly.[156] Bills[157] found that sunlight, but not indirect daylight, inactivates these organisms.

Weinstein[158] has given a curve (see Figure 134) for the relation between the wave-lengths used and the lethal action. It differs considerably from the analogous curves for bacteria in that the longer wave-lengths show greater effectiveness. In the case of such large cells there is some evidence to show that an optimum lethal action may occur closer to 2800A, the position of the maximum absorption by proteins, than to 2600A, that of the maximum absorption by nucleic acids. Leighton and Giese[159] have criticized the long wave-length limit indicated in the curve of Weinstein. They found that, although doses of only 16,500 ergs per sq. mm. sufficed to kill paramecia at 3025A within 24 hours after the irradiation, far greater dosages of the wave-length 3130A were ineffective. Doses as high as 191,000 to 200,00 ergs per sq. mm. had little if any effect. Weinstein had reported that the organism is killed about one-ninth as readily at 3130A as at 2654A and one-half as readily as at 3025A. Leighton and Giese attribute Weinstein's results to the presence of stray radiations, possibly the result of scattering within the quartz prism, in the light assumed to be of the wave length 3130A. In general, Leighton and Giese found that to produce vesiculation (their criterion of death) in 50 per cent of the cells, a large number of quanta, 10^{13}, must be absorbed by each paramecium.

Hutchinson and Ashton[160] employed monochromatic light (both visible and ultraviolet), and in their controls took into account the period of the growth curve at which the specimens were taken. They believed that certain frequencies in the red, yellow and near ultraviolet regions stimulated growth, and the green rays as well as ultraviolet rays shorter than about 3000A retarded growth or killed the cells. Effects were different during the early and later portions of a 24-hour irradiation in some cases.

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[150] Gilles, E., *Compt. rend. soc. biol*, **109,** 739 (1932); *Chem. Abs.*, **27,** 3969 (1933).

[151] Folger, H. T., *J. Exp. Zool.*, **51,** 261 (1925); Heilbrunn, L. V., and Daugherty, K., *Protoplasma*, **18,** 596 (1933); *Chem. Abs.*, **27,** 4849 (1933)

[152] Black, W. A., *Univ. Calif. Pub. Zool.*, **41,** 75 (1936); *Chem. Abs.*, **30,** 8254 (1936).

[153] Hughes, D. M., and Bovie, W. T., *J. Med Research*, **39,** 223, 233 (1918).

[154] Harris, F. I., and Hoyt, H. S., *Science*, **56,** 318 (1917).

[155] Bovie, W. T., and Daland, G. A., *Am. J. Physiol*, **66,** 55 (1920).

[156] Forbes, H. S., and Daland, G. A, *Am J. Physiol*, **66,** 50 (1923).

[157] Bills, C. E., *Biol. Bull. Marine Biol. Lab.*, **47,** 253 (1924).

[158] Weinstein, I., *J. Opt. Soc. Am.*, **20,** 433 (1930).

[159] Leighton, P. A., and Giese, A. C., *J. Gen. Physiol*, **18,** 557 (1934); *Science*, **81,** 53 (1935).

[160] Hutchinson, A. H., and Ashton, M. R., *Canadian J. Research*, **1,** 292 (1929).

Alpatov and Nastyukova[161] find *Paramecium caudatum* twice as susceptible to the stimulating and depressing actions of radiations as *Paramecium bursaria,* which contains green symbiotic algae. After the latter had been kept in darkness until the algae lost their color, the two species were equally susceptible. The addition of electrolytes which induce swelling in colloids decreased the resistance of the organisms to ultraviolet rays and those which shrink colloids made the organisms more resistant.[162] Increase in viscosity produced by an electric current increased the resistance and decreases in viscosity produced by chloretone decreased resistance to irradiation.

A latent period of several minutes to hours between the cessation of irradiation of *P. bursaria* and the death of many cells has been emphasized by Tang and Gaw,[163] who have discussed the effects of the age of the organisms upon the constants of an empirical equation for the survival curve.[164] Tchakhotine,[165] by means of an ultramicroscope, observed the flocculation of cell colloids by the passage of a sharp pencil of ultraviolet light into the cytoplasm of amoebae, paramecia, spyrogyra and other organisms. Localized flocculations of cytoplasmic proteins cannot be obtained. Nuclear substances change in dispersion but do not precipitate.

Eggs, Embryos, Lower Animal Forms. The oöcysts of *Eimeria tenella,* if unsegmented, suffer a 100 per cent mortality after a ten-minute exposure to a temperature of 53°, 15 seconds at 60° or to three quarters of a zinc sulfide unit of ultraviolet light.[166]

Lillie and Baskerville[167] found that exposure of unfertilized eggs of *Arbacia* to ultraviolet light for five to fifteen minutes caused membrane formation and cytolysis. The treated eggs, unless overirradiated, showed the usual increased susceptibility to hypertonic sea water. Even when the radiations had been too weak to produce membranes, the susceptibility to hypertonic sea water was increased. Hinrichs[168] found that regions of high physiological activity were modified first in development by radiations. These regions were also the first to recover from slight injury. Irradiation of the sperm reduced its motility, delayed cleavage and interfered with the normal development of the zygote. Loose sperm suspensions of *Arbacia* lost their fertilizing power more rapidly on irradiation than concentrated ones. The sperm was agglutinated.

Klugh[169] used filters in comparing the effects of various components of sunlight on a series of seven marine organisms which differed widely in their response to light. It was concluded that there is a fairly close relation between the depth at which the organisms live and their susceptibility to radiations of shorter wave-lengths. In several cases lethal effects were found even though all the radiations used were present in sunlight.

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[161] Alpatov, V. V., and Nastyukova, O. K., *Proc. Soc. Exp. Biol. Med.,* **32,** 99 (1934).

[162] Alpatov, V. V., and Nastyukova, O. K., *Compt. rend. Acad. Sci. U.R.S.S.,* **3,** 595 (1934); *Chem. Abs.,* **29,** 2182 (1935).

[163] Tang, P. S., and Gaw, H. Z., *Chinese J. Physiol.,* **11,** 305 (1937); *Chem. Abs.,* **31,** 4728 (1937).

[164] Early observations are due to Dreyer, G., *Mitt. Finsen's Lichtinstitut,* **4,** 81 (1903); **7,** 98 (1904); Hertel, E., *Z. Allgem. Physiol.,* **5,** 95 (1905); Sonne, C., *Arch. Phys. Therap. X-Ray, Radium,* **10,** 239 (1929).

[165] Tchakhotine, S., *Compt. rend.,* **200,** 2036 (1935); *Chem Abs.,* **29,** 587 (1935); *Boll. soc. ital. biol. sper.,* **4,** 475 (1929); *Trans. Faraday Soc.,* **33,** 1068 (1937), *Compt. rend.,* **206,** 133 (1938).

[166] Fish, F., *Science,* **73,** 292 (1931); *Chem. Abs.,* **25,** 2771 (1931).

[167] Lillie, R. S., and Baskerville, M. L., *Am. J. Physiol.,* **61,** 272 (1922).

[168] Hinrichs, M., *Biol. Bull. Marine Biol. Lab.,* **50,** 55, 473 (1926).

[169] Klugh, A. B., *Canadian J. Research,* **1,** 100 (1929).

Pigmented embryos of the nocturnal slug, *Limax flavus,* are easily injured by ultraviolet rays.[170] The deeply pigmented ones are especially sensitive.

The eggs and the first instar larva of the bean weevil, *Bruchus obtectus,* are killed by light of wave-lengths less than 3126A.[171] Adults showed no visible effects on irradiation, but most of their eggs were sterile. Sublethal doses produced weevils defective in metabolic processes.

Stevens [172] found that total arc exposure of the whole *Ascaris* egg for six or eight hours usually did not kill the egg at once, but prevented further development if the eggs had been in the two-cell or four-cell stage at the time of exposure. With shorter exposures, there was observed irregular fragmentation of the chromosomes, delay in cleavage and abnormal gastrulation. Schleip [173] irradiated various parts of the egg separately and concluded that no one part could be affected without producing some alteration in the unirradiated parts as well. Ruppert [174] found a rhythmic alteration in the lethal effect, depending on the stage of development of the egg when irradiated with energy of a wave-length of 2800A.[175]

Wright and McAlister [176] found ova of the roundworm of the dog, *Toxascaris Leonina,* to exhibit retarded embryonation after irradiation with the lines 2652 or 2804A at intensities of 684,000 ergs per sq. cm. They were particularly interested in the possible lethal action of sunlight, but found destructive effects only with the wave-length 3022A, but not with longer ones. Even at 3020A, 137,000,000 ergs per sq. cm., approximately equivalent to twelve days of July sunlight at Washington, D. C., caused only 1.5 per cent of the ova to reach embryonation, as compared with 42 per cent in the controls. For *Toxocara* ova, the corresponding figures were 20.5 per cent as compared with 65.5 per cent. The lesser susceptibility of this species may be due to absorption or dispersion of the light by the mosaically patterned, darkly pigmented shell of these eggs as compared with the clear, lightly pigmented shell of the *Toxascaris* ova. The ultraviolet rays of sunlight may be a factor, along with temperature and desiccation, in the marked lethal action of sunlight on ova reported by several workers.

APPLICATIONS

The Sterilization of Water. At one time sterilization by ultraviolet bid fair to be the method of choice for the treatment of water on a large scale and several installations were claimed to have been satisfactory. A description of the operation of an installation at Henderson, Ky., given by Smith,[177] states that there was little or no variation in the results, the rate of pumping being 2,200,000 to 3,200,000 gallons per day. The energy expenditure was said to have been 92.5 kilowatt hours per million gallons.

[170] Carmichael, E. B., *Physiol. Zool.,* **4,** 575 (1931).

[171] MacLeod, G. F., *Ann. Entomol. Soc. Am.,* **26,** 603 (1933).

[172] Stevens, N. M., *Arch. Entwicklungsmech. der Organismen,* **27,** 622 (1909).

[173] Schleip, W., *Arch. Zellforsch.,* **17,** 289 (1923).

[174] Ruppert, W., *Z. wiss. Zool.,* **123,** 103 (1924).

[175] Note also Seide, J., *Z. wiss. Zool.,* **124,** 252 (1925); *Chem. Abs.,* **20,** 1871 (1926); Nolf, L. O., *Am. J. Hyg.,* **16,** 288 (1932).

[176] Wright, W. H., and McAlister, E. D., *Smithsonian Misc. Coll.,* **93,** 1 (1934).

[177] Smith, A. T., *Eng. News Record,* 1021 (1917).

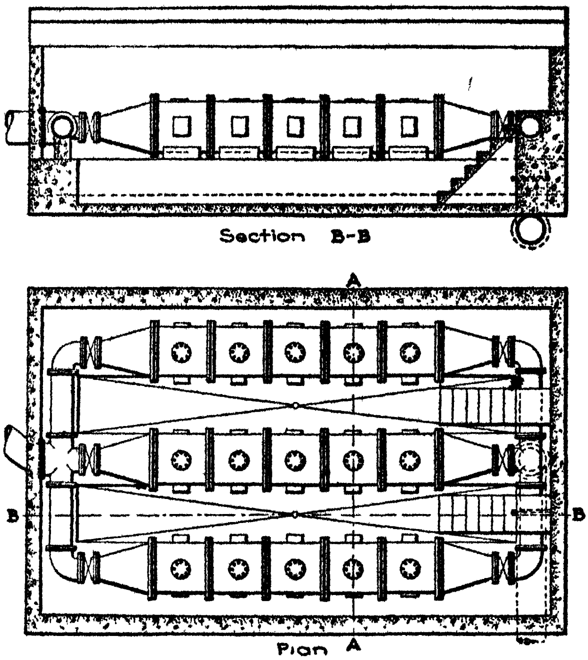

FIGURE 138 Large-scale Water Sterilization Equipment.

The ultraviolet sterilizers consisted of three legs each comprising five units. (Figure 138.) The legs were connected in parallel and the entire equipment was connected in series with a pipe line leading from the filtered water basin to the storage for the city supply. Each unit had a lamp box inserted in the side equipped with a clear quartz closed-end tube which projected into the body of the unit and around which the water was forced in a thin film by means of a baffle placed at 90° to the long axis of the sterilizer. The quartz tube was contained in a slotted opening in the baffle. (Figure 139.) The lamp proper was a 220-volt d.c. mercury arc designed to be automatically tilted for starting by a special support located in the lamp box. The individual lamps were so connected that they could be adjusted individually. They were also connected to the main switchboard, each lamp having an incandescent lamp and a warning bell to notify the operator of improper operation.

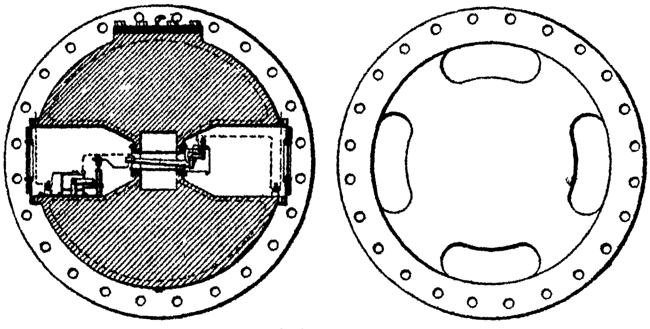

FIGURE 139. Lamp Box.

Blocher[178] states that the method was successfully in use at Berea, Ohio, in 1929 for the treatment of river water. The water was passed through four copper boxes in series, each of which contained a mercury-vapor lamp surrounded by a quartz cylinder.[179]

The advantages of the method are evident. The water itself undergoes no change. The materials in solution and the air, both of which give the water a pleasant taste, are retained. An overtreatment is not possible and the cost is not prohibitive. Springer,[180] although emphasizing that the water must first be clarified, believes the process to be superior to chlorination in that no disagreeable odor or taste is produced.[181]

Nevertheless, the method has declined in favor owing to the competition of the cheaper and in some respects simpler chlorination methods. For this reason working details of the apparatus employed will not be given, and reference will merely be made to the pertinent patents and articles in the field.[182]

Beattie[183] states that the treatment of natural waters is ineffective. During the early development of these methods it was occasionally stated that the treatment of water so alters it as to render it germicidal. Such statements were disputed,[184] but have been occasionally found in the subsequent literature. Norton[185] stated that water exposed to ultraviolet light retained a slight germicidal power toward typhoid bacilli and Friedländer's bacilli, but not toward staphylococci.

The use of ultraviolet rays for the purification of the water of swimming pools is no longer practiced extensively, principally because of the inability to make the necessary exposure of all the water to the radiations. Also, chlorination is reported to be cheaper and more effective.[186] Occasionally a favorable report of the method still appears.[187]

There are, however, several fields in which the method is useful because the chemical methods may be objectionable and an overdose harmful. Among these are the sterilization of water for surgical purposes under certain conditions, the sterilization of bottled waters, and other beverages (before bottling),[188] and the treatment of water intended for washing butter and for use in foods.[189]

Lloyd[190] claims that the exposure of filtered sea water to ultraviolet light for one second sterilizes it effectively. The cost of irradiation treatment is said to be about a hundred times that of chlorination.[191]

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[178] Blocher, J. M., *J. Am. Water Works Assoc.*, **21**, 1361 (1929); *Brit. Chem. Abs.*, **1929B**, 1034.

[179] Note also Rodriguez-Ely, *Tech. sanit. munic.*, **30**, 288 (1935).

[180] Springer, J. F., *Pub. Works*, **62**, 10, 36; **11**, 65 (1931); *Chem. Abs.*, **26**, 1048 (1932).

[181] See also Perkins, R. G., and Welch, H. [*Contract Journ.*, March 4, 1931; *Chem. Abs.*, **26**, 1997 (1932)] for a favorable opinion.

[182] Helbronner, A., and von Recklinghausen, M., British P. 4,895; 24,632; 28,067; 25,883; 21,829; 30,397, Dec. 29, 1909; French P. 424,369. Henri, V., Helbronner, A., and von Recklinghausen, M., U. S. P. 1,140,819, May 25, 1915; 1,200,940; 1,150,117, Aug. 17, 1915; Dornic, P., and Daire, P., *Chem. Ztg.*, 936 (1909); *Chem. Abs.*, **3**, 2988 (1909); Tassilly, E., and Cambier, R., *Compt. rend.*, **151**, 342 (1910); *Eng. Record*, 110 (1912); *Sci. Am.*, 515 (1917); Otto, M. P., French P., 421,296, Oct. 10, 1910; *J. für Gasbeleuchtung und Wasserversorgung*, **56**, 528 (1913); Perkin, F. M., *Trans. Faraday Soc.*, **6**, 199 (1911); Nogier, T., French P. 426,606, May 6, 1910; 420,281; British P. 9,960, April 20, 1911; von Recklinghausen, M., U. S. P. 1,156,947, Oct. 19, 1915; 1,193,209; *J. Soc. Chem. Ind.*, 976 (1916); Parkinson, N. F., *23rd. Ann. Rept. of Provincial Board of Health, Ontario, Canada*, **33**, 156 (1914); Keyes, F. G., U. S. P. 1,235,698, Aug. 7, 1917; Bruére, S., *Ann. Hyg. Pub., New Series*, **1**, 348 (1923); Dienert, F., *Ann. Hyg. Pub. Ind. Sociale*, 586 (1924); Sirch, C. W., U. S. P. 1,860,435, May 31, 1932; Baumgärtel, T., *Wasser und Abwasser*, **33**, 207 (1935); *Chem. Abs.*, **29**, 6677 (1935).

[183] Beattie, J. M., *Surveyor*, **78**, 69 (1930); *Chem. Abs.*, **26**, 1365 (1932).

[184] Cernovodeanu, P., and Henri, V., *Compt. rend.*, **150**, 52 (1910)

[185] Norton, J. F., *Am. J. Pub. Health*, **18**, 476 (1928); Vadimov, M., *Priroda*, **24**, No. 4, 13 (1935); *Chem. Abs.*, **31**, 7074 (1937).

[186] See Heath, R. F., *Can. Engr.*, **70**, No. 14, 27 (1936); *Chem. Abs.*, **30**, 7746 (1936).

[187] Turner, A. A., *J. Roy. Sanit. Inst.*, **55**, 441 (1935); *Chem. Abs.*, **30**, 1481 (1936).

[188] Schnegg, H., Kipphan, H., and Grunert, K., [*Z. ges. Brauw.*, **59**, 21 (1936); *Chem. Abs.*, **30**, 8513 (1936)] discuss its use in breweries.

[189] Stateler, E. S., *Food Ind.*, **7**, 535 (1935).

Residual chlorine and chloramine in distilled water drops markedly on exposure of the water to arc lamps, and the acidity increases in proportion to the reduction in free chlorine.[192] The *o*-tolidine reagent used in the free chlorine test becomes unreliable because of discoloration after exposure to direct sunlight for two months. Similar discoloration impairs the dichromate-copper sulfate standard.[193]

STERILIZATION OF FOOD PRODUCTS

Sterilization of Milk and Other Opaque Substances. After the introduction of ultraviolet sterilization, many patents describing processes for treating milk were issued. These will not be described in detail since the process apparently interferes with the irradiation of milk for the production of vitamin D, and because complete sterilization is difficult. Also the prolonged treatment necessary for sterilization is reported to have deleterious effects upon the flavor of the milk.[194] In the patent of Henri and von Recklinghausen, it was stated that heating the milk to 60°C. before irradiation would make the bacteria more sensitive to the action of the rays. In addition to the preheater (Figure 140) there was employed a rotating drum to pick up a very thin film of the milk, a procedure frequently used in irradiation of opaque fluids. von Recklinghausen[195] obtained a thin film by passing the liquid between two plates, one of quartz, the plates being separated by sheets of tin foil. Further patents dealt with details of methods for removing milk from rotating drums or rollers in such a manner as to avoid formation of particles of butter on the roller.[196]

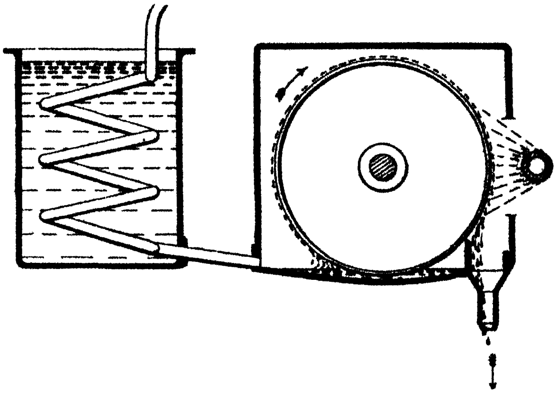

FIGURE 140. Apparatus of Helbronner and von Recklinghausen for Heat and Ultraviolet Treatment of Milk.

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[190] Lloyd, B., *J. Roy Tech. Coll.*, **3**, 505 (1935); *Chem. Abs.*, **29**, 4041 (1935).

[191] Vagedes, H., *Gas-und Wasserfach*, **78**, 80 (1935); *Chem Abs*, **32**, 1826 (1938).

[192] Buchanan, E. B, and Dodge, J. K., *15th Ann. Rept. Ohio Conf Water Purif*, 40 (1936); *Chem. Abs.*, **30**, 6859 (1936).

[193] Davis, W. S., and Kelly, C. B., *J. Am. Waterworks Assoc.*, **26**, 757 (1934); *Chem. Abs.*, **28**, 4807 (1934).

[194] Henri, V., and von Recklinghausen, M., U. S. P. 1,141,046, May 25, 1915.

[195] von Recklinghausen. M. U. S. P. 1,165,921, Dec. 28, 1915, *Chem. Abs.*, **10**, 649 (1916).

[196] Henri, V., Helbronner, A., and von Recklinghausen, M., U. S. P. 1,140,818, May 25, 1925; 1,068,898, July 29, 1913; 1,052,818, Feb. 11, 1913; Helbronner, A., and von Recklinghausen, M., British P. 12,948, May 27, 1910; 18,458, Aug. 4, 1910; for sterilizing fats and butter, note Soc. Le Serment, French P. 400,921, March 17, 1909.

Potencier[197] delivers milk under carbon dioxide pressure from a tank onto a metal or transparent table in a thin layer and collects the milk in a gutter surrounding the table. The rays are emitted from tubes situated under a parabolic cupola above the table. The cupola may be made either of polished metal or of insulating material faced on the inside with a fluorescent coating yielding rays between 2300 and 4500A. Scheidt[198] used a lamp in which a high-tension discharge is passed through neon and argon in a series of quartz tubes either U-shaped or formed of two coaxial vertical rims one enclosing the other. The rays are allowed to act on the liquid as it flows in a thin film between the surfaces of the quartz tubes and surrounding tubes of porcelain.

Vogeler[199] states that sterilization of milk by ultraviolet light is not a feasible process. Various attempts have been made to combine the use of ultraviolet rays with chemical treatments, using for example, hydrogen peroxide[200] or chlorine.[201]

Food Products.[202] The ingredients of jams, jellies, and other preserves may be subjected to the action of ultraviolet rays while being heated in a shallow pan provided with means for agitation and removal of the scum.[203] Perino[204] suggested that nutritive extracts of vegetables be irradiated in the absence of oxygen.

Spolverini[205] states that ultraviolet irradiation of certain foods causes physical and chemical changes which tend to aid conservation. Berndt and Creighton[206] treat the foodstuff with ultraviolet until beneficial properties have been imparted to a portion of the material, and mix this with untreated material. Apparatus designed for irradiation of viscous food products such as malt extracts has been described by Rohde.[207] Duret[208] finds ultraviolet sterilization of sugar solutions of value because occasional samples of sugar are found to contain thermophilic bacteria which resist heat sterilization.

Ultraviolet Sterilization in Baking Industry. In milling flour, it is usually necessary to remove the germ from cereals in order to prevent growth of organisms which lead to spoilage of the flour. To preserve these valuable portions of the grain, Mayor[209] proposes to irradiate the germ with ultraviolet rays, roast the treated germ, and mix the latter with the ground kernel of the same or other cereal.

In the bleaching of flour, mercury-arc irradiation is occasionally employed to supplement the action of such bleaching agents as dibenzoyl peroxide. By this means it is said to be possible to obtain in one hour the amount of bleaching that would be effected by allowing the peroxide to stand alone in contact with flour for 48 hours.[210]

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[197] Potencier, R., British P. 430,908, Dec. 21, 1933; *Brit. Chem. Abs.*, **B**, 827 (1935).

[198] Scheidt, E. O., British P. 257,956, Sept. 6, 1926; *Brit. Chem. Abs.*, **B**, 106 (1928); U. S. P. 1,670,217, May 15, 1928.

[199] Vogeler, L., *Milchwirtschaft Literaturber.*, 484 (1930); *Chem. Abs.*, **26**, 1039 (1932).

[200] Bing, M., German P. 392,935, 1922; *Brit. Chem. Abs.*, **B**, 345 (1927).

[201] Tranin, S., and Snyder, R. M., U. S. P. 1,945,102, Jan. 30, 1934; *Chem. Abs.*, **28**, 2428 (1934). Note for another recent milk patent, Castelain, L., U. S. P. 1,956,667, May 1, 1934.

[202] See Haines, R. B., Lea, C. H., Lea, D. E., and Tompkins, R. G., *Rep. Food Invest. Bd.*, 29, 1936; *Brit. Chem. Abs.*, **B**, 1264 (1937).

[203] McKinlay, D., British P. 273,578, Dec. 14, 1926; 272,775 (for fruits); *cf.* Mayor, J., U. S. P 1,911,913.

[204] Perino, J., British P. 279,487, Oct. 22, 1926; *Chem Abs*, **22**, 2799 (1928).

[205] Spolverini, L. M., *Riv. ital. actionol.*, **2**, 1 (1927); *Chem. Abs.*, **23**, 4508 (1929).

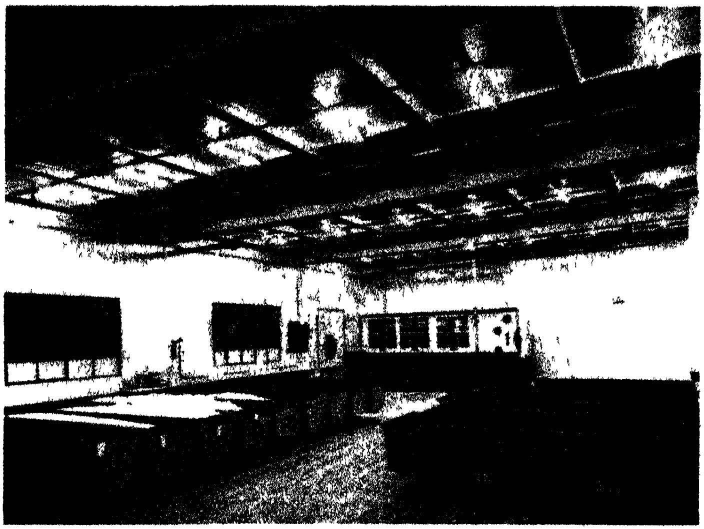
[206] Berndt, E. C., and Creighton, H. M., U. S. P. 2,072,416-7-8; *Chem. Abs.*, **31**, 2701 (1937).

[207] Rohde, H. W., U. S. P. 1,888,472, to Jos Schlitz Beverage Co.

[208] Duret, G., French P. 736,254, Aug. 13, 1931; *Chem. Abs.* **27**, 1540 (1933); British P. 395,527, July 20, 1933; *Chem. Abs.*, **28**, 362 (1934).

[209] Mayor, J., French P. 752,261, Sept. 20, 1933; *Chem. Abs.*, **28**, 838 (1934).

Read[211] studied the use of various sources of ultraviolet light in killing mold spores infecting the surface of freshly baked bread. He did not find the mercury-vapor arc to offer the advantages to be obtained by the use of the carbon arc. With various carbons, the fungicidal potency decreases in the following order: "C," "U," "K" and Mg. On the other hand it has been stated that growth of molds in bread can be checked by utilization of discharge lamps containing argon, neon and mercury.[212] Rooms in which dough is stored for yeast reaction are kept warm and moist and these conditions favor the growth of molds. It was reported that such growth could be inhibited by exposing dough to lamps emitting radiation between 2000-2600A. The rays were said not to penetrate beneath the surface of the dough, and to have no effect upon the yeasting process (Figure 141). Also, lamps which furnish rays in the range mentioned have been employed in the cooling and wrapping rooms of bakeries to prevent deposition of bacteria on bread subsequent to the baking process. Bonsor[213] subjected the dough ingredients during mixing to ultraviolet light for five or ten minutes to render the final product lighter and more easily digested.



Courtesy Westinghouse Electric and Manufacturing Co.

FIGURE 141. Use of Ultraviolet Radiation in Dough Room of a Bakery.

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[210] Ferrari, C. G., and Croze, A. B., *Cereal Chem.*, **11**, 505 (1934); *Chem. Abs.*, **29**, 236 (1935); Ferrari, C. G., Croze, A. B., and Bailey, C. H., *Cereal Chem.*, **9**, 491 (1932); *Chem. Abs.*, **26**, 6027 (1932); Sutherland, E. C., U. S. P. 1,539,701, May 26, 1925; *Chem. Abs.*, **19**, 2246 (1925); British P. 249,139, March 11, 1925; 102,967, Dec. 22, 1915; *Chem. Abs.*, **11**, 1219 (1917); U. S. P. 1,381,079, June 7, 1921; 1,380,334, May 31, 1921; *Chem. Abs.*, **15**, 3349 (1921); Gelissen, H., U. S. P 1 483,546, Feb. 12, 1924; *Chem Abs.*, **18**, 1167 (1924). In the earlier patents, other oxidizing agents, usually peroxides, were suggested.

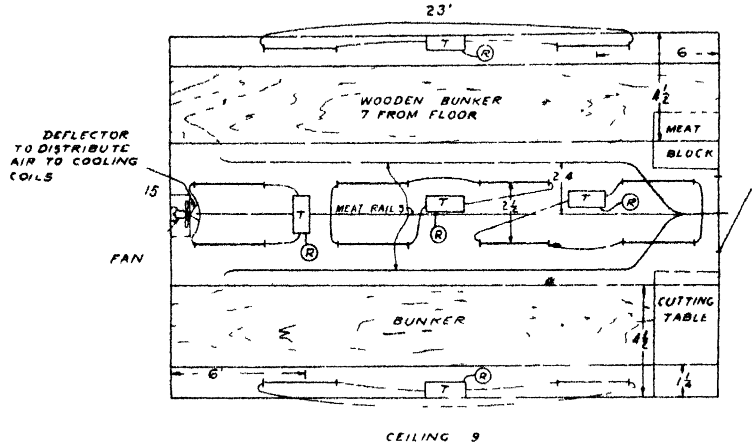
[211] Read, J. W., *Cereal Chem.*, **11**, 80 (1934); *Chem. Abs.*, **28**, 3142 (1934).

[212] Hibben, S. G., and Blackburn, P. W., *Electrical Engineering*, 455 (1938). Garrett, O. F., and Arnold, R. B., *Milk Plant Monthly*, August (1938). *Food Industries*, 10, (5), 263 (1938). James, R. F., *Food Industries*, 10 (6), 295 (1936). Dennington, A. R., *The Bakers Technical Digest*, March (1937). Broadbent, H. S., *Food Industries*, 10 (6) (1938).

[213] Bonsor, S., British P. 280,729, Dec. 16, 1926; *Brit. Chem. Abs.*, **B**, 106 (1928).

Ultraviolet Sterilization in Meat Industry.[214] Freshly slaughtered beef is composed of small muscle fibers 0.002 inch in diameter and 1 to 2 inches in length enclosed in a sheath-like covering. The muscle fibers are bound together into larger aggregates by connective tissue. When beef is stored, the connective tissue is changed to a gelatin by enzymic action within the meat. This process, called tendering, may be accelerated by increasing the temperature. However, temperatures above refrigeration limit (above 45°F.) also speed up mold formation on the surface of the meat, thereby causing considerable loss of the latter when the mold is cut away.

Also, storing of meat may result in considerable shrinkage by evaporation of moisture when the relative humidity of the storage room is below 83 per cent. A relative humidity of 85-90 per cent in the vicinity of stored meat was stated to prevent evaporation from meat to a large extent. These highly moist conditions tend to accelerate mold formation.



Courtesy Westinghouse Electric and Manufacturing Co.

FIGURE 142. Use of Ultraviolet Lamps in Meat Storage Rooms.

The presence in a storage room of rays of about 2000-2600A was advocated as effective in inhibiting mold formations on meat surfaces, at temperatures above 35°F. and relative humidity of 85 90 per cent.[215] Lamps emitting these radiations generally are placed in rows parallel to the racks or rails on which meat is hung for storage or tendering (Figure 142). Also, it is reported that circulation of air in the storage room prevents mold formation in areas where meat is not exposed directly to rays from discharge lamps.

Miscellaneous Applications. Ultraviolet sterilization has been proposed as efficient for destroying bacteria on eating and drinking implements.[216] Exposure of glasses (after washing and rinsing) to rays from discharge lamps was reported to result in destruction of 87-100 per cent of the bacteria present.

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[214] Ewell, A. W., *Refrigerating Engineering*, January (1939). Coulter, M. D., Address at Mellon Institute of Industrial Research, March 21, 1939. British P. 22,669, 1914, to Monvoisin, Barrat et Robin; *Chem. Abs.*, 10, 1238 (1916).

[215] Lamps utilized for this purpose are known as Sterilamps (Trade Mark Registered U. S. Patent Office), manufactured by Westinghouse Electric & Manufacturing Co.

[216] R. V. Fellers, *The American City*, August, 53 (1938).

In the sterilization of fruit juices, Welch and Perkins[217] suggested the use of the photosensitizing action of eosin or fluorescein, only very small concentrations being required.

The condition of pitched barrels or casks is reported to be greatly improved, even though complete sterilization is not attained, by lowering quartz lamps into them and irradiating them for fifteen to thirty seconds. Longer periods may heat the casks to such an extent as to cause the liberation of the fumes of pitch.[218]

STERILIZATION OF MEDICINAL PRODUCTS

Vaccines. It was early proposed to treat vaccinia virus by ultraviolet rays, the belief being that harmful foreign organisms could be killed by doses insufficient to destroy the more resistant virus.[219] Kirstein,[220] using the Vitaray apparatus, was unable to find any evidence of such action. Later, however, he introduced a process using a salicylic acid filter, which he claimed accomplished this purpose not in the case of the vaccinia virus, but in the preparation of various bacterial vaccines. The killing of the organisms was said to be accomplished by filtered ultraviolet rays.[221]

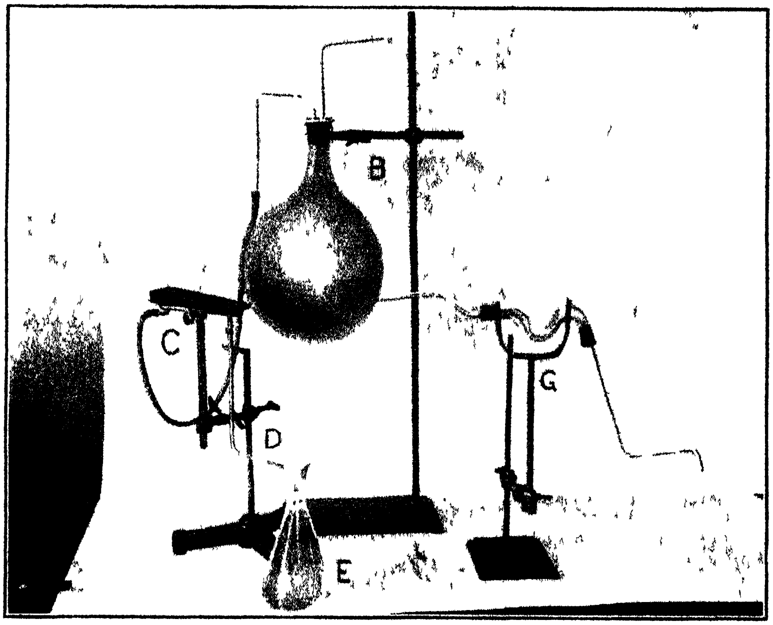

FIGURE 143 Apparatus of Hougton and Davis for Sterilization of Vaccines.

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[217] Welch, H, and Perkins, R G, *J Prev Med*, **5,** 173 (1931), *Chem Abs* **26,** 5362 (1932).

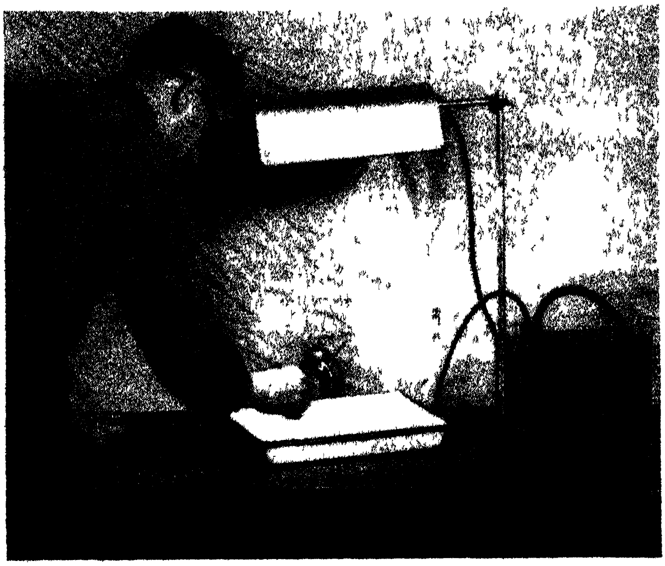
[218] *Sci Am*, 201, Aug. 28, 1920; Moufang, E, *Allgem. Z. Bierbrau Malzfab*, **43,** 151 (1915).

[219] German P. 314,858, Feb. 24, 1914, to Quarzlampen Ges Hanau, *J. Soc Chem. Ind.*, **39,** 312 (1920); Friedberger, E., and Mironescu, E, *Deut Med. Wochschr* 1203 (1914), Mayerhofer, E, *Z Kinderheilk*, **13,** 361 (1916).

[220] Kirstein, F., *Zentralb. Bakt. Parasitenk. Infektionsk.*, **I, 114,** 530 (1929)

[221] Kirstein, F, German P. 598,680, June 15, 1934, *Chem Abs*, **28,** 5932 (1934), German P. 600,941, Aug 3, 1934; *Chem. Abs.*, **28,** 7433 (1934), German P 609,258, Feb 11, 1935, *Chem. Abs.*, **29,** 6366 (1935). Note also Mayer, G., German P. 505,707, April 3, 1927, *Chem. Abs.*, **25,** 382 (1931).

Figure 143 illustrates apparatus used by Houghton and Davis [222] for sterilizing bacterial vaccines and other products. The material to be irradiated is contained in a glass flask B connected by a sterile glass siphon and rubber tubing to the trough C placed directly beneath the arc. After exposure in the trough, the liquid passes through the delivery tube D into a previously sterilized container E. A modern quartz mercury arc suitable for irradiating the liquid in the trough is shown in Figure 144.



Courtesy Dr. L. J. Buttolph, Lamp Department, General Electric Co.

FIGURE 144. Modern Quartz Mercury Arc for Irradiation of Liquids.

Pharmaceutical Products. Lesure [223] found it possible to sterilize several drug preparations without altering them, although in several cases the absorption by the drugs was so great as to prevent effective sterilization within a reasonable time. Silver nitrate, eserine salicylate, apomorphine hydrochloride and atoxyl all became colored after five minutes of exposure and morphine hydrochloride, arbutin and guaiacol cacodylate after fifteen to thirty minutes. Arbutin became colored after three hours because of the formation of quinol and its oxidation products.

Sperti, Norris, Withrow and Schneider [224] proposed to employ only selected radiations, obtained by the use of filters of, for example, lead acetate, in destroying bacteria in enzyme solutions without affecting the enzyme activity. They also suggested that selective irradiation might be employed for activation of vitamins and for differentially affecting organic substances having several ingredients.

Mingoia [225] found it impossible to sterilize solutions of such alkaloids as heroine, cocaine, atropine and codeine by irradiation so as to render them suitable for hypodermic use without at the same time altering the alkaloids seriously. Nitzescu[226] believed that insulin solutions could be sterilized in this manner.[227]

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[222] Houghton, E. M., and Davis, L., *Am. J Public Health*, 4, 224 (1914).

[223] Lesure, A., *J. pharm. chim.*, 1, 569 (1910); *J. Chem Soc.*, 98, 739 (1910).

[224] Sperti, G., Norris, R. J., Withrow, R., and Schneider, H., U. S. P. 1,676,579, July 10, 1928

[225] Mingoia, Q , *Ann. chim applicata*, 23, 318 (1933); *Chem. Abs.*, 27, 5889 (1933).

Kelly[228] proposed the sterilization by irradiation of certain emulsions used in ointments and shaving creams.

In treating substances serving as sources of essential oils, Tival and Descombes[229] first froze the material, then irradiated it and dried it *in vacuo* before extracting the oil. Rousseau[230] added uranium, iron or manganous salts to enzymes or yeast before subjecting the latter to the action of ultraviolet rays.

According to Stevens,[231] ultraviolet light renders the lipids of skin, extracted and emulsified in salt solution, bactericidal to hemolytic streptococci. It increases markedly the active oxygen content of dried skin, unless the lipids had been extracted before irradiation.

Various Products. Wool which has been treated with ultraviolet light is said[232] to have increased susceptibility to mold growth. Gelatin solutions and articles made from them, such as threads, cords, violin strings, ribbons, or tubes, may be sterilized by ultraviolet light, according to Hirsch.[233] Redd[234] describes apparatus for subjecting clothes to ultraviolet rays and ozone in laundry apparatus.

Lehmann[235] finds that staphylococci in contact with linoleum die more rapidly under strong illumination than when irradiated on glass or wood. This is ascribed to the action of oxidation products of the linseed oil present in the linoleum.

Considerable attention has recently been devoted to the bactericidal properties of irradiated petrolatum. Eising[236] noted that the latter exerted a strong bactericidal action upon the ordinary organisms of wound infection and believed it also to stimulate the processes of healing. Sheard and Thompson[237] found irradiated mineral oil less active than irradiated olive oil or Vaseline. Harris, Bunker and Milas[238] found the vapors of certain oils to inhibit or kill bacterial smears on nutrient agar without irradiation, although other oils acquired this power only after being irradiated. They believed the germicidal action due probably to volatile substances containing peroxidic oxygen in the oil, the formation of which is accelerated by irradiation, the most effective rays being about 3130A. In general, animal oils were more active than vegetable oils. The germicidal properties are not the result of secondary radiations, aldehydes, butyric acid or ozone. Sears and Black[239] observed that white petrolatum becomes germicidal after four hours of irradiation and changes to a limpid yellow color. The germicidal agent is believed to be a nonvolatile chemical substance, not water-soluble, formed as the result of oxidation. It does not kill spores or certain gram-negative intestinal organisms. Stevens[240] attributed the photoactivity of such products to the evolution of gaseous organic peroxides and aldehydes which diffuse rapidly through a film of cellulose acetate. The plate-fogging and bactericidal effects of the vapor from irradiated cod-liver oil and from ozonide of olive oil were found to be due to substances liberating active oxygen. Not only are bacteria killed by the oxygen liberated from these oils, but their growth rate may be retarded or dissociation may occur if the organisms are subjected to sublethal doses.

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[226] Nitzescu, I. I., *Klin. Wochschr.*, **3**, 2343 (1924); *Chem. Abs.*, **19**, 1285 (1925).

[227] See, however, Chapter 34.

[228] Kelly, T. D., British P. 283,711, Dec. 13, 1926; *Chem. Abs.*, **22**, 4205 (1928).

[229] Tival, H., and Descombes, F., British P. 179,164, April 25, 1922; *Chem. Abs.*, **19**, 1019 (1925).

[230] Rousseau, E. F., British P. 226,534, Dec. 17, 1923; *Chem. Abs.*, **19**, 2103 (1925).

[231] Stevens, F. A., *J. Exptl. Med.*, **65**, 121 (1937).

[232] Burgess, R., *J. Soc., Dyers Colourists*, **50**, 138 (1934); *Chem. Abs.*, **29**, 1992 (1935).

[233] Hirsch, P., British P. 299,105, July 25, 1927; *Chem. Abs.*, **24**, 3061 (1929).

[234] Redd, W. R., U. S. P. 1,948,239, Feb. 20, 1934, to Millprint Products Corp.; *Chem. Abs.*, **28**, 2923 (1934).

[235] Lehmann, K. B., *Arch. Hyg.*, **106**, 1 (1931); *Chem. Abs.*, **26**, 166 (1932).

[236] Eising, E. H., *Annals of Surgery*, **93**, 1231 (1931); British P. 417,685, Oct. 10, 1934; *Chem. Abs.*, **29**, 1211 (1935). U. S. P. 1,919,055, July 18, 1933; *Chem. Abs.*, **27**, 4879 (1933).

[237] Sheard, C., and Thompson, L., *Proc. Staff Meeting Mayo Clinic*, **6**, 690 (1931); *Chem. Abs.*, **26**, 2764 (1932).

[238] Harris, R. S., Bunker, J., and Milas, N., *J. Bact.*, **23**, 429 (1932); *Ind. Eng. Chem.*, **24**, 1181 (1932).

[239] Sears, H. J., and Black, N., *J. Bact.*, **27**, 453 (1934).

[240] Stevens, F. A., *J. Lab. Clin. Med.*, **21**, **26**, 1040 (1935-6); *J. Bact.*, **32**, 47 (1936); *J. Inf. Dis.*, **58**, 185 (1936).

Courtesy Westinghouse Electric and Manufacturing Co

FIGURE 145. Ultraviolet Sterilization of Air in Operating Room.

Reiner-Deutsch and Molnar[241] found irradiation of essential oils in alcohol for fifteen minutes at 25 cm. from a Burdick air-cooled lamp to increase their bactericidal power so that the vapors would kill staphylococci in three hours.

It has been claimed that irradiated metals are bactericidal at a distance[242]

Utilization of Ultraviolet Sterilization in Hospitals.[243] The degree of contamination in an operating room is said to depend on the duration of occupancy, number of occupants in the room, the number of contamination carriers and the degree of contamination in their respiratory passages, the adequacy of masks, the cleanliness of the room and of the incoming air, and the efficacy of the ventilating system. It was found that careful regulation of the above factors to afford maximum protection against entrance of bacteria did not achieve this purpose completely. Members of the operating team constantly breathe bacteria into the air, even though all members wear masks. Presence of bacteria is particularly dangerous in thoracic surgery, where long incisions are made. For this reason, thoracic operations seldom were performed during winter months, when the probability of respiratory contamination in the operating team was highest. The observations of Rentschler and James[244] that air-borne pathogenic bacteria can be killed with about 10 per cent of the radiant energy required to kill the same bacteria on a plate led to a method for controlling bacteria in operating rooms. In one type of installation proposed by James and Hart (Figure 145) a bank of eight lamps which emit principally the line 2537A is arranged in a square above the operating table. Rays from these lamps kill bacteria (breathed by members of the operating team) before the bacteria reach the body of the patient. It was stated that the intensity of the ultraviolet rays reaching the operating table is too low to cause harmful aftereffects to the patient. Further, utilization of such lamps was reported to accelerate wound healing.

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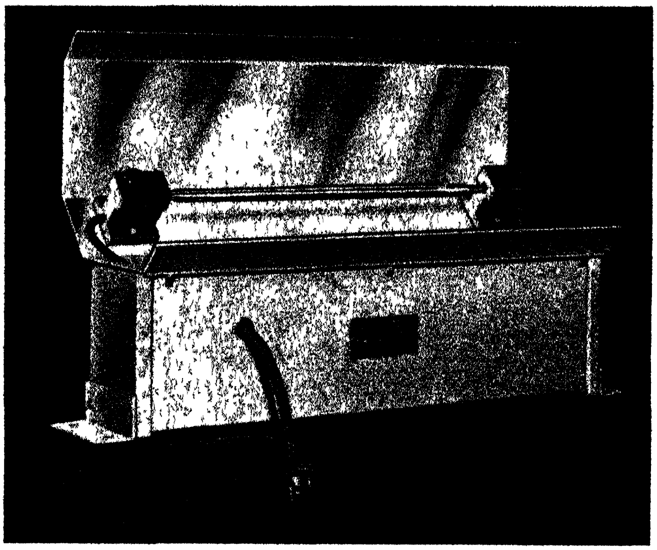
[241] Reiner-Deutsch, W., and Molnar, N., *J. Bact*, **30**, 444 (1935); *Chem. Abs.*, **30**, 1086 (1936).

[242] Ried, O, *Centralbl. Bakt. Parasitenk.*, *Abt. I*, **121**, 267 (1931); Goldberg, I. M, *Acta. Med Skand.*, **83**, 212, 573 (1934).

[243] Hart, D., *J. Thoracic Surg.*, **6** (1), 4581 (1936) Hart, D., *Surgery*, 1 (5), 770 (1935). Hart, D, *Archives of Surgery*, **34**, 874 (1937). Hart, D, and Gardner, C E, Jr, *Transactions of the Southern Surgical Associations*, **49**, 377 (1937). Hart, D., *J. Thoracic Surg.*, **7** (5), 525 (1938). Hart, D, *Archives of Surgery*, **37**, 956 (1938). *The Modern Hospital*, **46** (6), June (1936). Hibben, S. G, and Blackburn, P. W., *Electrical Engineering*, 455 (1938).



Courtesy Hanovia Chemical and Manufacturing Co.

FIGURE 146 Operating Room Safe-T-Aire Equipment for Ceiling or Wall Mounting.

The effectiveness of bactericidal radiation during extrapleural thoracoplasties has been studied. It was found that mortality was reduced more than 50 per cent by use of radiation during operations, that postoperative infection was avoided almost completely, that postoperative temperature elevations of patients decreased and that wound healing was more rapid. Also, the period required before reopen-

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[244] Rentschler, H. C., and James, R. F., in article of Hibben, S. G., and Blackburn, P. W., *Electrical Engineering*, 455 (1938). Rentschler, H. C., Address at Mellon Institute of Industrial Research, March 21, 1939.

FIGURE 147 (*a*).

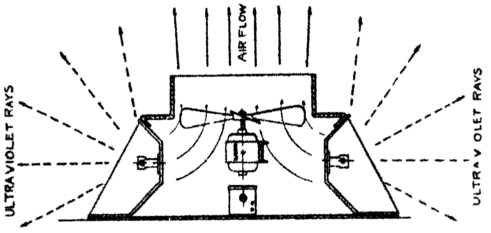
Baryaire Safe-T-Aire Equipment.

Courtesy Hanovia Chemical and Manufacturing Co.

FIGURE 147 (*b*).

Baryaire Safe-T-Aire Equipment.

Courtesy Hanovia Chemical and Manufacturing Co.



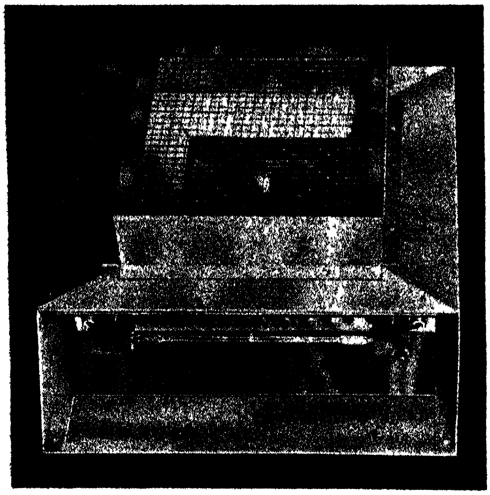


FIGURE 147 (*c*).

Courtesy Hanovia Chemical and Manufacturing Co.

ing of the wound to complete the stages of thoracic surgery was reported to be lessened considerably.

Wells and Brown[245] found it possible by means of the mercury arc to destroy the infectivity for ferrets of the influenza virus (P R 8 strain) suspended in air. Other quartz operating room lamps have been designed (Figure 146) for ceiling or wall mounting. "Baryaire" units (Figure 147) have been devised for use in hospital corridors to prevent cross-infection. It is claimed that microörganisms cannot be carried past the barrier of ultraviolet light.[246]

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[245] Wells, W. F., and Brown, H. W., *Am. J. Hyg.*, 24, 407 (1936); see also Wells, W. F., and Wells, M. W., *J. Am. Med. Assoc.*, 107, 1698, 1809 (1936).

[246] Note also Magondeaux, B., French P. 729,022, March 9, 1932.

Chapter 36

The Physiological Effects of Ultraviolet Rays

The success attained in the use of ultraviolet light in the treatment of rickets, surgical tuberculosis and certain other conditions discussed in subsequent chapters, stimulated a widespread empirical (and frequently non-critical) use of this treatment for a great variety of diseased conditions. Unwarranted and extravagant claims served to create an undeserved prejudice against even the proper application of this form of therapy. For this reason, before discussing in Chapter 38 the therapeutic applications in which ultraviolet light may serve a useful purpose, it is desirable to consider the present state of our knowledge of the general physiological effects of this form of energy upon multicellular organisms. The preceding chapters have laid the basis for this by enumerating the effects of the rays upon the chemical constituents of cells and upon individual cells as a whole. The way in which generalized irradiation of large areas of the body may produce alterations in the circulation, respiration, the composition of the blood and the growth of the body as a whole or of various of its organs may now be considered.*

In the extensive literature many apparent contradictions abound.

In part, these may be ascribed to inaccurate observations or to too hasty generalizations from an inadequate number of experiments. In part, they are due to a failure to appreciate the necessity of controlling the spectral distribution of the sources employed. Much work calls for repetition under more adequate physical control. In the present survey, it has not been considered possible to undertake a detailed analysis of the adequacy of the experimental approach in the various investigations reported, since for the most part the results are not usually striking. A more critical treatment would demand a much larger amount of space than is justifiable in view of the fact that there are at present available several reviews and books. Only an outline of what appear to be the more significant conclusions is given here.[1]

Comparatively little work has as yet been done on the application of the Einstein law to biological systems, aside from that involved in the photosynthetic mechanism in plants and in the formation of vitamin D_2.[2] There is thus a hiatus between the photochemical theories discussed and applied in Part II of this book and the treatment of the photochemical processes upon which must ultimately depend the physiological responses which occupy a large part of the remainder of this book.

Early workers were inclined to the belief that ultraviolet rays act in some manner by virtue of photoelectric effects, produced when they strike the living organism.[3] This is now recognized to play a role of importance only when the wavelengths employed are far shorter than those available from the sources usually employed under the ordinary conditions of experimental work or practical therapy.[4]

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* The conversion of sterols into vitamin D and its application is deferred to Chapters 38, 39 and 40.

[1] Laurens, H., "The Physiological Effects of Radiant Energy," American Chemical Society Monograph Series, New York, Reinhold Publishing Corp., 1933; "The Biological Effects of Radiation." Edited by Duggar, B. M, 2 Vols., New York, McGraw-Hill Book Company, Inc., 1936.

Review articles· Valentin, H., *Pharm. Ztg.*, **75**, 982, 995, 1005 (1930); *Chem. Abs.*, **25**, 120 (1931); Levine, V. E., *Arch. Phys. Therapy, X-Rays & Radium*, **12**, 197, 267, 389 (1931); Packard, C., *Quart. Review Biol.*, **6**, 253 (1931); Snyder, C. D., *Ibid.*, 281; Frankenburger, W., *Strahlentherapie*, **27**, 233 (1933); de Toni, G., *Biochim. terap. sper.*, **22**, 547, 577 (1935); **23**, 75 (1936).

[2] Warburg, O., *Trans. Faraday Soc.*, **27**, 551 (1931).

Attention has been drawn by various workers to the possibility that x-rays or radium may owe some of their biological actions to ultraviolet rays produced as a result of the fluorescence of some components of the irradiated systems. As yet this possibility has been relatively little explored.[5]

There have been, among the many suggestions advanced to account for the general reactions underlying the utility of heliotherapy or artificial ultraviolet therapy, a few which have attained special prominence, at least for a time. One group of workers advanced the claim that the effects were due, not to the direct effects of the light rays upon the body surface, but rather to the production in the air of ozone or oxides of nitrogen which when breathed were indirectly responsible for the effects produced. A leading sponsor of this theory was Kestner,[6] who had in mind particularly the use of a carbon arc source. Peemöller[7] asserted that only when the air through which the rays passed was breathed was it possible to observe any effect of the irradiation upon the blood pressure. This theory has been discredited by subsequent workers who have shown that the effects of irradiation on blood pressure cannot be detected if the subject (a dog) is exposed to the irradiated air but protected by filters from the direct action of the rays.[8]

Another view was that physiological alterations may ensue as a result of a stimulation through the eye of the nervous control of the circulation. There is an experimental basis for this in the observation by Reed that in the dog[9] strong irradiation of the retina produces a depression of the blood pressure, usually accompanied by a decrease in the heart rate, which eventually leads to a condition of shock unless the irradiation be discontinued. Nevertheless, there is little reason to believe that under ordinary conditions the reaction of the body to irradiation is brought about by nerve stimulation in the eye and this may be dismissed from further consideration.

Current theories regard the behavior as a response to changes brought about in the skin. Most of the radiations are absorbed in very thin layers of the skin and do not penetrate to the lower tissues. One process which occurs in the skin, the conversion of certain sterols into the vitamins of the D group is definitely known to account for the beneficial results of irradiation in the prevention and treatment of rickets, and there is an accumulating body of evidence that this may also account, in part at least, for the beneficial results in tuberculosis. There are, however, undoubtedly other processes induced in the skin which are less well understood. The visible changes in sunburn have been attributed to the production of histamine-like materials which then act upon the vessel walls and produce the local erythema. Such substances may enter the blood stream and be carried to the nervous tissues which control the fundamental physiological processes. Such substances may also conceivably exert a control through a local stimulation of certain afferent nerves. Viale and Roncallo[10] find that although irradiation of a normal rabbit's foot depresses the blood sugar, this effect is not found if the nerves to the foot are first cut. Furthermore, section of the right vagus nerve at the neck also interferes with the fall in blood sugar which usually follows irradiation.[11]

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[3] Clark, J., *Physiol. Rev.*, **2**, 277 (1922).

[4] See, however, Saidman, J., *Compt. rend.*, **180**, 693 (1925); Gallerani, G., *Boll. soc. ital. biol. sper.*, **11**, 817 (1936); *Chem. Abs.*, **31**, 7759 (1937).

[5] See Spiegel-Adolf, M., *Klin. Wochschr.*, **9**, 1615 (1930).

[6] Kestner, O., *Z. Biol.*, **73**, 1, 7 (1921); **77**, 245 (1922).

[7] Peemöller, F., *Klin. Wochschr.*, **2**, 973 (1923); note also Secchi, C., *Pediatria Rivista*, **35**, 1111 (1927); *Chem. Abs.*, **22**, 1786 (1928).

[8] Laurens, H., and Mayerson, H. S., *Am. J. Physiol.*, **84**, 524 (1928).

[9] Reed, C. I., *Am. J. Physiol.*, **65**, 477 (1923).

[10] Viale, G., and Roncallo, E., *Boll. soc. ital. biol. sper.*, **10**, 311 (1935); *Chem. Abs.*, **30**, 6014 (1936).

Other views assume that light absorbed by the blood in dilated skin capillaries alters its constitution. Others view the circulatory effects as due primarily to the shift of blood into dilated skin capillaries, that is to a localized hyperemia. This view is particularly advanced in explaining the results of the longer wave-lengths used in heliotherapy. Sonne[12] made determinations of skin and subcutaneous temperatures during irradiation, as a result of which he concluded that the visible and shorter infrared rays produce local temperatures greater than those observed in fevers. His work is of importance in affording some measure of explanation of the differences in the effects produced by sunlight and carbon arc light from those due to the mercury arc which produces less of these rays and more of the short ultraviolet rays.

Another group of German workers regard the effects of general irradiation as due to a generalized protein shock similar to that after the injection of milk or other non-specific proteins. The shock is assumed to result from the introduction into the circulation of the products produced by the destruction of proteins in the cells of the skin. This is particularly adapted to the explanation of the effects following mercury-arc irradiation.

Rothmann[13] believed the general response due to a lowering of the tone of the sympathetic system.

EFFECTS ON THE SKIN[14]

During exposure of the skin to sunlight, an immediate reddening is usually observed. This is a heat erythema due to the longer visible and infrared rays. It is not strictly localized in the irradiated parts and disappears shortly after the irradiation is stopped.

The erythema due to the ultraviolet rays of sunlight is produced only after a latent period of from one to ten hours. It is seen only in the irradiated areas and varies in severity with the intensity and duration of the exposure, blistering accompanying the more intense or longer doses. The erythema persists for several days and is then replaced by an area of pigmentation, the upper epidermal layers scaling off. The pigmentation may persist for several months. These effects were first described in detail by Finsen who employed a carbon arc as the source of light.

During the erythema there is a widening of the capillary blood vessels and at its height, there is leucocytic infiltration and degeneration, particularly of the cells of the Malpighian layer. These later dry to a scale above a regenerated pigmented skin.[15]

Ultraviolet radiations are highly absorbed by the skin. Exact measurements of their penetrability are difficult because a portion of the shorter wave-lengths are converted by fluorescence into longer ones in the blue and other portions of the visible region and these have greater penetrability. Vlès and Ugo[16] find the fluorescence spectrum of shaved rat skin to be in part that of the proteins and in part that of cholesterol. Pauli[17] states that the fluorescence curve is to a large extent coincident with the erythema curve. Rabbit skin shows a fluorescence between 5400 and 4200 with a maximum at 5000A. That of human skin has its maximum at 4600A.

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[11] Martini, E., and Roncallo, E., *Boll. soc. ital. biol. sper.*, **11**, 77 (1936); *Chem. Abs.*, **30**, 6063 (1936).

[12] Sonne, C., *Acta Med. Skand.*, **54**, 336 (1921); **56**, 619 (1922); *Acta Radiologica Skand.*, **5**, 419 (1926); *Chem. Abs.*, **21**, 1139 (1927).

[13] Rothmann, H., *Klin. Wochschr.*, **2**, 881 (1923); Petersen, W. F., and v. Oettingen, W. F., *Arch. Exptl. Path. Pharmakol.*, **123**, 160 (1927).

[14] *Cf.* Waller, M. D., *Proc. Roy. Soc.*, **108B**, 259 (1931), and for a general discussion, Eidinow, A., *Brit. J. Tuberculosis*, **22**, 136 (1928).

[15] For histological details, see Keller, P., *Strahlentherapie*, **16**, 52 (1924); **28**, 152 (1928); Uhlmann, E., *Ibid.*, **40**, 765 (1931). See also Rost, G. A., and Keller, P., in Jadassohn, "Handbuch der Haut und Geschlechtskrankheiten," Vol. 2, Berlin, J. Springer, 1929.

[16] Vlès, F., and Ugo, A., *Compt. rend. soc. biol.*, **123**, 226 (1936); *Chem. Abs.*, **31**, 713 (1937).

Hasselbalch[18] gave the results indicated in Table 24 for the penetration of the rays from a Kromayer water-cooled quartz mercury lamp. Anderson and Macht,[19] who agreed that dead skin is practically opaque to wave-lengths shorter than 3660A, claimed that live rabbit skin has a much greater transparency, transmitting from 6 to 10 per cent of the energy at wave-lengths between 2537 and 3000A. Bachem and Reed,[20] however, were able to find but little difference between live and dead skin if the specimen was kept moist and tightly stretched. They found the wave-lengths of the near infrared and visible regions strongly absorbed by the blood of the corium and subcutaneous layers. The far infrared rays have very little penetrating power and are absorbed in the epidermis. Some of their data are reproduced in Figure 148. The absorption of a band with maximum at 2800A is very great in the corneum and prickle cell layers. On both sides of this band near 3000 and 2500A, the penetration is greater, more radiation reaching the Malpighian layers and the corium.

Table 24.—Penetration of Rays from Kromayer Lamp.

	Wave Length in Millimicrons							
	436	405	366	354	313	302	297	289
Per cent transmitted by skin 0.1 mm. thick	59	55	49	42	30	8	2	0.01
By skin 1.0 mm. thick	0.5	0.3	0.08	0.02	0.006			

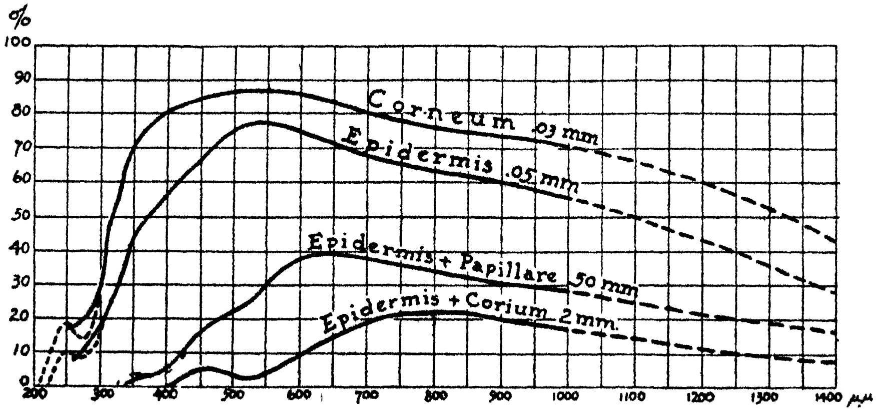

FIGURE 148. Transmission Curves for the Various Skin Layers (Bachem and Reed, *American Journal of Physiology*).

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[17] Pauli, W. E., *Strahlentherapie*, **26**, 577 (1927); *Chem. Abs.*, **22**, 3672 (1928).

[18] Hasselbalch, K. A., *Skand. Arch. Physiol.*, **25**, 55 (1911); *Chem. Abs.*, **5**, 2862 (1911).

[19] Anderson, W. T., Jr., and Macht, D. I., *Am. J. Physiol.*, **86**, 320 (1928).

[20] Bachem, A., and Reed, C. I., *Am J. Physiol.*, **97**, 86 (1931); **90**, 600 (1929).

Bachem[21] has also given data on the ultraviolet transparency of the various layers of the human skin. Figure 149 indicates that the horny layer is very transparent in the visible and near ultraviolet. At 3000A a strong absorption band begins, which has its maximum at 2800A and then diminishes to a minimum at 2600A, increasing again at shorter wave-lengths, and recalling the absorption of the proteins. The granulosum layer absorbs somewhat more visible light. Most transparent is the germinating layer. The corium differs in showing the greatest absorption for the visible light. It also shows no absorption maximum at 2800A and has somewhat lower absorption coefficients in the more extreme ultraviolet range. Bachem believes the erythema to originate in the stratum germinativum or corium under the shadow of the upper layers.

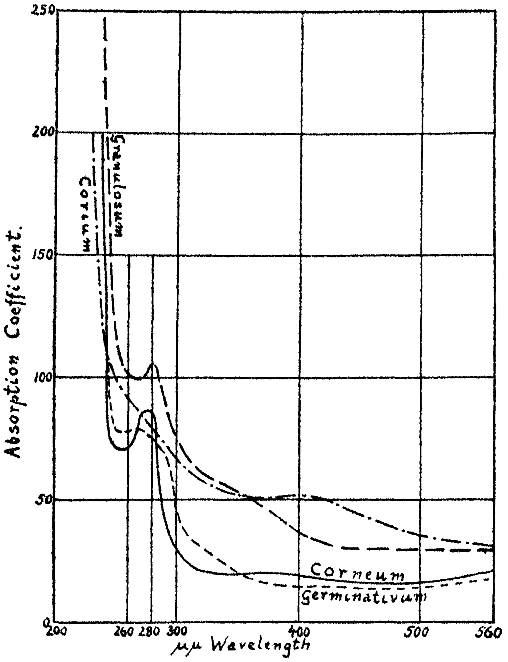

FIGURE 149. Absorption Curves for Various Skin Layers (Bachem, *American Journal of Physiology*).

Lucas[22] has discussed particularly the difficulties involved in this type of measurement. He expressed his results merely in terms of the relation between the logarithms of incident and transmitted light. His observations indicated the skin used to be a hundred to ten thousand times more opaque than that studied by Hasselbalch, much of the loss of radiant energy being due to scattering. In the living animal, however, much of the scattered light may not be lost to the animal. Lucas was unable to detect the passage of any line shorter than 3130A through 0.2 mm. of skin in exposures less than 24 hours. With very thin specimens of epidermis obtained from blisters of the forearm, Lucas obtained the results of Figure 150, which appear to resemble greatly the curves for the absorption of the amino- acids, tryptophane and tyrosine. These observations appear chiefly of value in demonstrating the extreme difficulty of the problem of measuring the absorption of the skin as a whole, since they had to be limited largely to the epidermis. They do, however, demonstrate that the penetration of ultraviolet rays cannot be more than very slight. Pauli[23] claims that glycerol containing a little alcohol is the best agent for increasing the ultraviolet permeability of the skin.

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[21] Bachem, A., *Am. J. Physiol.*, **91**, 58 (1929).

[22] Lucas, N. S., *Biochem. J.*, **25**, 57 (1931).

By the use of a monochromator, Hausser and Vahle[24] determined the relative degrees of erythema produced by the various mercury-arc lines, each being adjusted to the same intensity. They found a maximum sensitivity at 2970A, the effect beginning at 3130A. Wave-lengths in the visible and longer ultraviolet had no effect. Adopting the intensity of the erythema produced by the 2970A line as 100 per cent, the relative values found on irradiation by the other wave-lengths were found to be as indicated in Table 25. In later work, they found a second maximum

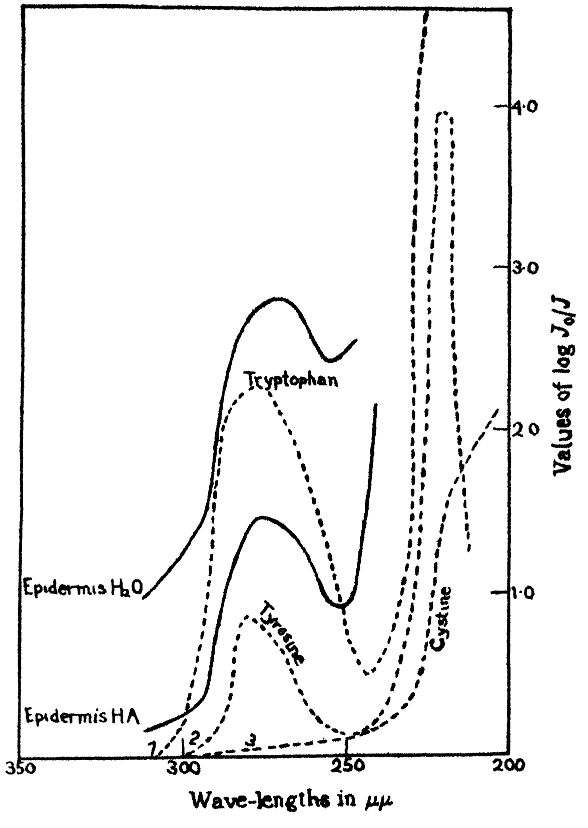

FIGURE 150. Absorption of Skin from a Blister (From Lucas, *Biochemical Journal*).

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[23] Pauli, W. E., *Strahlentherapie*, **26**, 577 (1927); *Chem. Abs.*, **22**, 3672 (1928).

[24] Hausser, K. W., and Vahle, W., *Strahlentherapie*, **13**, 41 (1921); **27**, 348 (1928); Henri, V., and Moycho, V., [*Compt. rend*, **158**, 1509 (1914)] early placed the maximum irritating effect on rabbit's ear at 2800A.

Table 25.—Effect of Wave-Length on Erythema.

Wave-Length (A)	Erythema (%)
Greater than 3130	None
3130	4.5
3020	58.
2970	100.
2890	30
2800	28

at 2500A. Luckiesh, Holladay and Taylor,[25] using a filter method, confirmed the existence of the maximum at 2970A but found at the shorter wave-lengths values which tended to increase steadily from a minimum at 2800A to 2400A, the shortest wave-length studied. They also studied the reflectance of the skin for various wave-lengths and found it very low for wave-lengths shorter than 3100A. The erythema results of Coblentz, Stair and Hogue[26] tended, however, to resemble more closely the values of Hausser and Vahle than those of Luckiesh, Holladay and Taylor at the region near 2540A. Figure 151 compares the results of these workers.

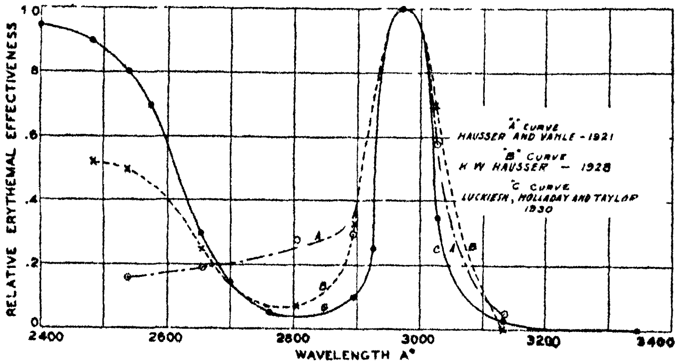

FIGURE 151. Relative Erythemal Effectiveness of Equal Amounts of Radiant Energy at Various Wave-lengths. Curve A, according to Hausser and Vahle, 1921; B, according to K. W. Hausser, 1928; C, according to Luckiesh, Holladay and Taylor, 1930. (Luckiesh, Holladay, and Taylor, *Journal Optical Society of America*).

The energy required to produce a minimal perceptible erythema on a sq. cm. of untanned skin by the wave-length 2970A is, according to Coblentz, Stair and Hogue, of the order of 500,000 ergs. There is considerable variation in different persons and in different parts of the body of a given person.[27]

Luckiesh and Taylor[27a] find that to produce tanning, exposures to artificial or natural sunlight sufficient to give an appreciable erythema are required. Repeated suberythemal doses usually do not tan, although they may be effective in the cure of rickets. With an S-4 sunlamp emitting chiefly narrow bands at 2967, 3022 and 3130A, an exposure of four minutes at a distance of 2.5 feet was found necessary to produce on the human arm a minimal perceptible erythema visible one day after the irradiation. To produce a minimal perceptible tanning visible two months later, an exposure of 7.5 minutes was required. These authors also give a curve showing the relative tanning effectiveness of various wave-lengths. It is in general similar to the erythema curve except at the regions on either side of the maximum. Wave-lengths of 2500-2600A are ineffective in tanning, although they may cause a strong erythema. There is some evidence that wave-lengths longer than 3300A may produce immediately after exposure a brownish pigmentation with but little inflammation. This is of little practical significance since the energy densities and times of exposure required are prohibitive.

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[25] Luckiesh, M., Holladay, L. L., and Taylor, A. H., *J. Opt. Soc. Am.*, 20, 423 (1930).

[26] Coblentz, W. W., Stair, R., and Hogue, J. M., *Bureau Standards J. Research*, 7, 723 (1931); 8, 541, 759 (1932).

[27] See also Adams, E. Q., Barnes, B. T., and Forsythe, W. E., *J. Opt. Soc. Am.*, 21, 207 (1931); Uhlmann, E., *Strahlentherapie*, 35, 361 (1930); Hausser, K. W., and Schlechter, E., *Ibid.*, 27, 348 (1928); Keller, P., *Ibid.*, 34, 129 (1929); 35, 353 (1929).

[27a] M. Luckiesh and A. H. Taylor, *J. Am. Med. Assoc.*. 112. 2510 (1939).

MECHANISM OF THE PRODUCTION OF ERYTHEMA AND PIGMENTATION

It must be noted that the maximum of erythema production at 2970A corresponds to the absorption maximum of no known cell constituent, notwithstanding the observations of Lucas upon the epidermis alone, in which there was observed a fair degree of similarity to the absorption of proteins. That the wave-length of greatest absorption lies in the region of the least formation of erythema has been interpreted by Hausser and Vahle and by Bachem to indicate that erythema is a process effected in the deeper layers rather than in the epidermis. There is evidence that the erythema produced by wave-lengths of 2500A differs in character from that produced at 2970A in the shade of redness particularly. The reaction to the shorter rays is produced more rapidly and is more transient than that due to the longer ones and, for the same degree of redness, results in less pigmentation, provided the exposure to the short rays is insufficient to produce a severe and lasting burn.

Frankenburger[28] noted that the absorption of tryptophane and tyrosine occurs at wave-lengths about 200A on the short wave-length side of the erythema curve. He points out, however, that in alkaline solutions, the absorption of tyrosine at least is shifted to the longer wave-lengths in closer correspondence to the erythema curve. Since this shift is due to salt formation of the phenolic hydroxyl group, it could conceivably also occur when the amino- acid is bound in a protein. For a given incident energy, he calculated the energy effectively absorbed by the tyrosine contained in 80 micra of epidermis beneath 25 micra of corneum and compared it with that of alkaline tyrosine solutions in concentrations roughly equivalent to those in the tissues examined. From the marked similarity of the resulting curves he concluded absorption by tyrosine to be essential to the production of erythema. Although the tyrosine absorbed only from 4 to 13 per cent of the total incident energy at 2970A, it was believed that this was sufficient to produce the erythema. Frankenburger also irradiated 0.4-per cent aqueous solutions of *l*-tyrosine in quartz tubes with unfiltered light from a mercury arc. In air-free water no chemical or spectrographic changes could be detected within six hours. But in the presence of air, the tyrosine quickly changed through a yellow to a deep brown color and carbon dioxide was evolved. Frankenburger believed, as many have, that tyrosine forms first oxindo- compounds and then melanins which are components of the pigment of the skin. During irradiation the absorption increased and extended into the visible region in agreement with the spectra of melanins. Spiegel-Adolf obtains photosynthetic melanins by irradiating tyrosine or tryptophane in alkaline solution or phenylalanine in neutral solution.[29]

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[28] Frankenburger, W., *Naturwiss.*, 21, 116 (1933).

[29] Spiegel-Adolf, M., *Biochem. J.*, 31, 1303 (1937).

That the process underlying erythema formation is not that of a simple protein coagulation was the conclusion of Clark[30] from a comparison of the temperature coefficients of the two types of reaction. That for erythema formation is 2.3 in human and 1.9 in frog skin, but that of the coagulation of proteins (at least in its second stage) is very high, being over ten.

The production of melanin by irradiation of the skin has been effected by Lignac,[31] but irradiation of four minutes produced the same amount of pigmentation in live skin as several hours of irradiation in dead skin.[32] Schmalfuss, Bussmann and Nickelsen[33] believe skin contains other dye-forming substances than tyrosine, capable of darkening without enzymes in light. Intense solar irradiation of a normally pigmented individual causes the appearance of a melanin reaction, the Thormaehlen reaction, in the urine, but this is not observed in the case of previously irradiated and tanned individuals.[34]

The administration of vitamin C does not affect the pigmentation of human beings following ultraviolet irradiation, according to von Drigalski.[35] On the other hand, Schade[36] believed the daily administration of this vitamin for ten days after irradiation with an Alpine lamp prevented subsequent pigmentation. Balakhovskii[37] claimed the application of carotene in water or dilute alcohol to be beneficial in curing ultraviolet burns.

Lewis has long considered histamine or histamine-like substances of importance in the production of erythema, whether by irradiation or by heat, mechanical or electrical causes.[38] The mechanism of their liberation by irradiation does not appear to be a nervous one, since erythema may be produced after the nerves supplying the skin have been cut. Novocaine injected intradermally does lessen erythema formation, but this may be due to an internal filtering action. Krogh[39] believes that, although histamine may be formed, the predominant dilating compound in ultraviolet erythema must be a material of extremely low diffusibility. Otherwise it would diffuse into the blood through the enormous surface of the dilated blood vessels and thus be lost.

In a preceding chapter, mention was made of the belief of Ellinger that histamine may be photochemically produced by the decarboxylation of histidine. Frankenburger, however, pointed out that the absorption of histidine is great only at wave-lengths too short to permit the erythema curve to be accounted for by a direct action on histidine. He did, however, suggest that when this amino- acid is bound in peptide linkages, its absorption spectrum might be sufficiently displaced toward the longer wave-lengths to permit some absorption and photochemical change. He also described the production of a new absorption band at 3150 to 3200A during the irradiation of histidine solutions in the absence of oxygen. This new absorption did not resemble that of histamine, and histamine itself when irradiated also exhibited a new type of longer wave-length absorption. From his observations it would appear that in irradiated histidine solutions, histamine could at best be present in very slight concentrations, probably insufficient to account for the vasodilatation of erythema. Ellinger[40] found no difference in effects on the blood pressure of the cat or on the surviving guinea pig intestine of extracts prepared from skin before and after ultraviolet irradiation. Frankenburger concludes that the erythema reaction is a complex one, since strong erythema can be produced in the range of wave-lengths (3100 to 2750A) which fail to affect histidine. Accordingly, if histamine or some other erythema-producing substance is formed it must be indirectly produced. He also suggested that the changes induced in tyrosine are accompanied by changes in the protein of which it forms a part and that these are of a nature which increases the permeability of the membranes releasing substances of histamine-like nature normally present in cells.

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[30] Clark, J., *Am. J. Hyg.*, **24**, 334 (1936).

[31] Lignac, G., *Nederland Maanschr. Geneesk.*, **16**, 496 (1930); *Chem. Abs.*, **24**, 1873 (1930).

[32] See also Lovisatti, N., [*Forsch. Geb. Röntgenstrahlen*, **44**, 235 (1931); *Chem. Abs.*, **25**, 5679 (1931)] for the function of the melanotic pigments in increasing the ultraviolet tolerance.

[33] Schmalfuss, H., Bussmann, G., and Nickelsen, O., *Arch. Dermatol. Syphil.*, **175**, 39 (1937); *Chem Abs.*, **31**, 5422 (1937).

[34] Risak, E., and Asperger, H., *Klin. Wochschr.*, **11**, 154 (1932); *Chem. Abs*, **26**, 3553 (1932).

[35] von Drigalski, W., *Klin Wochschr.*, **13**, 1374 (1934); *Chem. Abs.*, **29**, 1138 (1935); Tenchio, F., *Klin. Woch.*, **13**, 1511 (1934); *Chem. Abs.*, **29**, 1139 (1935).

[36] Schade, H., *Klin. Woch.*, **14**, 60 (1935); *Chem. Abs*, **29**, 4045 (1935).

[37] Balakhovskii, S, *Compt. rend. acad. sci. U R.S S.*, **1**, 28 (1934); *Chem. Abs.*, **28**, 2736 (1934).

[38] Lewis, T., "The Blood Vessels of the Human Skin and Their Responses," London, Shaw and Sons, 1927.

[39] Krogh, A., "The Anatomy and Physiology of the Capillaries," New Haven, Yale University Press, 1929.

Various workers have attempted to correlate the temperature of the skin when irradiated with the severity of the effects produced. Thus, Shattock and Waller[41] believe that if the tissues are heated simultaneously with or shortly after exposure, the erythema is delayed or suppressed. On the other hand, exposure to heat before the irradiation increases the erythema produced. Hill[42] and Eidinow also believed that hyperemia tends to increase the effects of irradiations with the quartz lamp. Schall and Alius,[43] and Cramer and Fechner,[44] however, found little if any such effect.

Lehner and Urban[45] observed that repeated exposure of a definite area of normal skin produced after the first few treatments a more prompt and intense reaction, but after about three treatments there was little itching and scarcely any hyperemia. At the same time the spot so treated became less sensitive to other irritants, such as the injection of morphine. Ten minutes after the exposure of the entire back to the lamp, the skin of the breast or upper arm was more sensitive than normally to the injection intracutaneously of morphine solutions, but this hypersensitivity persisted for only thirty minutes. It has been stated that by giving repeated doses the skin may be induced to develop a tolerance to ultraviolet light so that the sensitivity may be reduced to as low as 8 per cent of its normal value for the individual. The filtering action of the pigments produced may play some part in this acquired tolerance, but other factors are probably concerned. Relatively little is known exactly about the production of tolerance. Antibodies do not seem to be concerned.

Sensitization of the skin has been observed. After rats have been injected intraperitoneally with chlorophyll, the erythema and hyperemia produced on irradiation of a portion of the skin were much more pronounced than in uninjected animals, according to Fulchignoni.[46] There has also been reported a case in which an alcoholic solution of chlorophyll when rubbed on the skin penetrated to the deeper layers and sensitized it so that a short exposure of the treated part to red or to ultraviolet light produced erythema, although the surrounding untreated parts were unaffected[47] Proft[48] found some soaps to increase the erythema due to light. This he believed to be independent of the presence of a sensitizing dye such as chlorophyll or the pigment of linseed oil, and also independent of the horny epithelium. Instead, he believed it due to the presence of free alkali. A weakened erythma results from the use of oils, fats and undissolved soaps and absolute protection was afforded by a 10-per cent alcoholic salicylic acid solution. The pH of the skin alters its light sensitivity, according to Marchionini and Hövelborn,[49] who found that pretreatment with a salve of pH 27 increased its sensitivity. Skin treated with an alkaline salve required two and a half times as much exposure as the acid-treated skin to produce an erythema. Papcke[50] believes peroral administration of an isotonic mixture of calcium, potassium and magnesium salts to decrease the erythemic response.

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[40] Ellinger, F., *Arch. Exp Path Pharmakol.*, **149,** 343 (1930).

[41] Shattock, F., and Waller, M. D., *Lancet*, **II,** 917 (1929).

[42] Hill, L., and Eidinow, A., *Lancet* **II,** 299 (1924); see also Török, L., Lehner, E., and Urbán, F., *Krankheitsforsch*, **5,** 293 (1927); *Chem. Abs.*, **22,** 4167 (1928)

[43] Schall, L., and Alius, H. J., *Strahlentherapie*, **26,** 649 (1927); **27,** 769 (1927-8).

[44] Cramer, H., and Fechner, G., *Ibid*, **39,** 474 (1931).

[45] Lehner, E., and Urbán, F., *Krankheitsforsch*. **4,** 381 (1927); *Chem Abs*, **22,** 4166 (1928).

[46] Fulchignoni, F., *Boll soc. ital. biol. sper.*, **11,** 428 (1936); *Chem. Abs.*, **31,** 1053 (1937).

[47] Kitchevatz, M., *Compt. rend. soc biol*, **116,** 675 (1934); *Chem. Abs.*, **28,** 5839 (1934); *Ann. de Dermat. et Syph.*, **5,** 293 (1934)

[48] Proft, H., *Strahlentherapie*, **40,** 351 (1931); *Chem Abs.*, **25,** 3675 (1931).

[49] Marchionini, A., and Hövelborn, C., *Arch. Dermatol. Syphilis*, **174,** 251 (1936); *Chem. Abs.*, **30,** 7591 (1936).

Irradiation of the skin of the guinea pig previously injected with methylene blue decolorizes it irreversibly. The skin of the frog similarly colored is decolorized in darkness but the color is restored on irradiation.[51] Wohlgemuth and Sugihara[52] found suitable irradiation of a guinea pig with natural or artificial sunlight to cause in the skin an increase of the enzyme phenolase, some decrease in lipase and a notable decrease in diastase. The blood enzymes were not affected. Other workers have shown therapeutic doses of ultraviolet light to affect the intracellular oxidase, peroxidase and catalase of the skin. Natural sunlight injures somewhat the ability of the skin to produce lactic acid, but artificial sunlight is more injurious and x-rays even more so.[53] Harpuder[54] found irradiation of the skin up to beginning erythema to affect the diffusion of chloride, calcium and potassium ions. Changes in the contents of water, sodium, potassium and calcium in the pigmented skin of rabbits after its irradiation by ultraviolet rays proceed in the same direction and reach the same values as in unpigmented skin.[55] The contents of sugar and glycogen in pigmented skin are less than in unpigmented skin, but the changes on irradiation proceed alike. No habituation could be observed in the changes in mineral and carbohydrate metabolism of the skin after irradiation.

Skin irradiated with ultraviolet light shows an increase in cholesterol content of from 7 to 150 per cent, according to Roffo.[56] The skin from various parts of the face contains from two to seven times as much cholesterol as skin from the abdomens of the same persons, and the distribution in the face is roughly proportional to the amount of exposure to the sun. Roffo also believed that there was a direct relationship between the frequency of skin tumors and the proportion of cholesterol in the skin. If white rats are kept in darkness there is a lowering of the cholesterol content of the skin.[57] These results were confirmed by Kawaguchi.[58]

Loewy and Cronheim[59] find that the non-protein nitrogen of rat or guinea-pig skin is not affected by five hours of irradiation. The chlorine content decreased either in darkness or under ultraviolet irradiation. Potassium was lowered by irradiation and unaffected by darkness in the rat but increased in guinea-pig skin. Magnesium was increased by irradiation but the calcium content was not altered. Beck[60] claimed local applications of a Vitrisol preparation made by prolonged irradiation of spinach gave good results in the treatment of acne vulgaris and lupus vulgaris. In the repair of cutaneous lesions, cholesterol has the greatest healing action, followed by irradiated ergosterol and then ergosterol.[61] It has been stated that in scleroderma, treatment with massive doses of the vitamin reduces the abnormal calcium deposits from the skin before that element is removed from the bones.[62] The antigen-antibody reaction in skin is inhibited by ultraviolet irradiation, according to Albus and Feldermann.[63] The total glutathione of rabbit skin appears to be increased following irradiation, probably because of a disintegration of tissue proteins.[64]

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[50] Papcke, G., *Arch. Dermatol Syphilis*, **168**, 476 (1933); *Chem. Abs.*, **28**, 525 (1934).

[51] Dubouloz, P., and Rochette, J., *Compt. rend. soc. biol.*, **122**, 221 (1936); *Chem. Abs.*, **31**, 3069 (1937).

[52] Wohlgemuth, J., and Sugihara, N., *Biochem Z.*, **163**, 260 (1925).

[53] Wohlgemuth, J., and Ikebaka, T., *Biochem. Z.*, **186**, 43 (1927); *Chem. Abs.*, **21**, 3632 (1927).

[54] Harpuder, K., *Z. ges. Exptl. Med.*, **76**, 724 (1931); *Chem. Abs.*, **26**, 4834 (1932).

[55] Kaplanskii, S. Y., and Kaplanskaya-Raiskaiya, S. I, *Arch. sci. biol. (U.S.S.R.)*, **39**, 169, 175 (1935); *Chem. Abs.*, **30**, 7185 (1936).

[56] Roffo, A. E., *Bol. inst. med exptl estudio cancer, No. 39*, 358, 390 (1935); Roffo, A. H., Jr., *Ibid.*, **41**, 41 (1936); *Chem. Abs.*, **31**, 4347 (1937); *Bol ist. Med. Exptl*, **6**, 370 (1929); *Chem. Abs.*, **26**, 1304 (1932); *Compt. rend.*, **201**, 566 (1935)

[57] Roffo, A. H., *J. Physiol. Path Gén.*, **29**, 739 (1931); *Chem Abs.*, **26**, 2993 (1932); *J. physiol. Path. Gén.*, **30**, 345 (1932); *Chem. Abs.*, **26**, 5330 (1932); *Bol. inst. med. exptl.*, **8**, 32 (1931); *Chem. Abs.*, **29**, 5871 (1935); *Arch. elect. med.*, **42**, 425 (1934); *Chem. Abs.*, **31**, 6682 (1937); Roffo, A. E., Jr., *Bol. inst med. exptl. estudio cancer*, **14**, 447 (1937); *Chem. Abs.*, **32**, 3812 (1938).

[58] Kawaguchi, S., *J. Biochem Japan*, **15**, 111 (1932); *Chem. Abs.*, **26**, 2995 (1932); see also Chorozak, T., *J. Physiol. Path. Gén.*, **31**, 408 (1933); *Chem. Abs.*, **28**, 3473 (1934).

[59] Loewy, A., and Cronheim, G. *Biochem. Z.*, **256**, 411 (1932).

[60] Beck, H., *Münch, med. Woschr.*, **74**, 1129; *Chem. Abs.*, **22**, 4655 (1928). For the use of Viosterol in acne, see Doktorsky, A., and Platt, S. S., *J. Am Med. Assoc.*, **101**, 275 (1933).

[61] Tautini, E., *Sperimentale*, **89**, 712 (1935); *Chem Abs.*, **30**, 7696 (1936); see Kemmler, H., *Mitt. Grenzg. Med. Chir.*, **43**, 453 (1934); *Chem. Abs.*, **29**, 5927 (1935).

[62] Cornbleet, T., and Struck, H. C., *Arch. Dermatol. Syphilol.*, **35**, 188 (1937); *Chem. Abs.*, **31**, 1487 (1937).

[63] Albus, G., and Feldermann, F., *Klin. Wochschr.*, **17**, 1702 (1938); *Chem. Abs.*, **32**, 6677 (1938).

Sunburn Creams and Protective Salves. A great number of skin creams for the prevention of sunburn are on the market and some contain materials which simulate a tan.[65] Malowan[66] states that the ointments which protect fluoresce strongly in ultraviolet light. Prominent constituents are naphtholsulfonic acid, and esculin and its homologs. Eder and Freund[67] propose salves or emulsions containing in addition to esculin or naphtholsulfonic acid, lithopone or a compound of titanium. Dunning[68] suggested the use of the sodium salt of a mono- or di-sulfonic acid of *o*- or *p*-hydroxybiphenyl. Hall[69] employs a polyhydric alcoholic ester of salicylic acid, such as glycerol or glycol mono-salicylate with a mineral oil, or with stearic acid, lanolin, beeswax, etc. Stockelbach[70] employs menthyl salicylate in a vehicle of alcohol, an oil or a cosmetic cream for preventing sunburn. Risler[71] mixed a phosphorescent zinc sulfide with about six times as much of a cream phase made by heating and mixing together stearic acid 170, glycerol 210, water 569, and 10-per cent aqueous ammonia, 50. When cold, one part of violet essence was added.

The I. G. Farbenindustrie[72] proposed such substances as aryl benzimidazoles or aryl benzothiazoles. Issermann, Ohlsson and Orelup propose about 0.5 to 1 per cent of an amino- or substituted amino-benzoic acid, as benzylamino-*o*-benzoic acid, in peanut or almond and mineral oils.[73] Jordan suggests dibenzalacetone as an effective component.[74]

In the past, quinine bisulfate was frequently employed in salves to act as an internal filter.[75] Other materials specified in the I. G. Farbenindustrie patents included stilbene, 2-phenylindole, α-phenylcinnamonitrile, 2-phenylquinoline, N-acetylcarbazole, μ-methylnaphthoxazole and 2-acetyl-3-bromoindazole. Schwarz suggests a cream containing oak bark extract.[76] Sodium phenylbenzimidazolesulfonate or other substances with sharp absorption of wave-lengths in the range 3200 to 3500A are claimed by Merkel and Wiegand to absorb noxious rays without excluding tanning rays.[77]

It has been claimed that sunburn does not follow exposure after vitamin C has been given intravenously and bergamot oil has been applied to the skin.[78]

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[64] Matusis, I. I., and Grechanovskiĭ, *Bull. biol. med. exptl. U.R.S.S.*, **3**, 489 (1937); *Chem. Abs.*, **32**, 8449 (1938).

[65] For general discussions see: Lendle, A., *Pharm. Ztg.*, **81**, 903 (1936); Stambovsky, L., *Drug and Cosmetic Ind.*, **36**, 551, 554 (1935); Van Itallie, P. H., *Drug Trade News*, **12**, No. 8, 41, 44, 45, 47 (1937); Augustine, J., *Riechstoff Ind. Kosmetik*, **11**, 218 (1936); Karl, P., *Ibid.*, **12**, 92 (1937); Goodman, H., *Am. Perfumer*, **34**, No. 6, 47 (1937); Böhme, H., and Reichert, B., *Arch. Pharm.*, **275**, 437 (1937); Kalisch, J., *Drug Cosmetic Ind.*, **42**, 52 (1938); Heber, C. F., *Svensk Kem. Tids.*, **50**, 144 (1938); Calame, A., *Seifensieder-Ztg.*, **65**, 456 (1938); Gattefossé, *Parfumerie moderne*, **32**, 97, 113 (1938).

[66] Malowan, L. S., *Seifensieder-Ztg.*, **61**, 335, 353 (1934); *Chem. Abs.*, **28**, 4836 (1934).

[67] Eder, J. M., and Freund, L., Austrian P. 138,527, Aug. 10, 1934; *Chem. Abs.*, **29**, 558 (1935).

[68] Dunning, F., U. S. P. 2,015,005, Sept. 17, 1935; *Chem. Abs.*, **29**, 7587 (1935).

[69] Hall, R. A., U. S. P. 2,081,117, May 18, 1937, to Colgate-Palmolive-Peet Co.; *Chem. Abs.*, **31**, 5111 (1937).

[70] Stockelbach, F. E., U. S. P. 2,041,874, May 26, 1936; *Chem. Abs.*, **30**, 5000 (1936).

[71] Risler, J., U. S. P. 1,779,891, Oct. 28, 1930; *Chem. Abs.*, **25**, 174 (1931).

[72] French P. 770,912, Sept. 24, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, **29**, 892 (1935); British P. 435,811, Sept. 30, 1935.

[73] Issermann, S., Ohlsson, E., and Orelup, J. W., U. S. P. 2,102,712, Dec. 21, 1937; *Chem. Abs.*, **32**, 1410 (1938).

[74] Jordan, A., German P. 652,929, Nov. 10, 1937; *Chem. Abs.*, **31**, 1410 (1938).

[75] See Hazen, H. H., *Am. J. Nursing*, **38**, 791 (1938).

[76] Schwarz, H., *Seifensieder-Ztg.*, **64**, 518 (1937); *Chem. Abs.*, **31**, 6413 (1937).

[77] Merkel, E., and Wiegand, C., U. S. P. 2,104,492, Jan. 4, 1938; *Chem. Abs.*, **32**, 1869 (1938).

[78] Urbach, E., and Kral, F., *Klin. Wochschr.*, **16**, 960 (1937); *Chem. Abs.*, **31**, 8015 (1937).

Secerov[79] found that after five to forty hours of exposure to ultraviolet rays the hair of a white guinea pig became yellow. In rats the production of alopecia by thallium is said to be reduced or retarded by the action of ultraviolet rays, which also accelerate the regeneration of hair in the bald spot.[80]

Light may be concerned in the production of argyria, the deposition of silver in the skin, after internal administration of silver salts.[81] The same may also be true of chrysiasis, the deposition of gold, after prolonged treatment with the gold compound, Sanocrysin.[82]

METABOLISM AND CIRCULATION

Only after very intense irradiation is the general body temperature elevated. When a sufficient amount of tissue damage has been done there may be a fever similar to that which follows the injection of protein destruction products. The effects of irradiation upon the basal metabolism are of little importance. During irradiation it may be increased by as much as 18 per cent, but it quickly returns to normal on the cessation of irradiation and remains unchanged during the erythema state.[83] Harris[84] found that ultraviolet radiation exerts a stimulant action on the gaseous metabolism of small animals and on the movements of the isolated stomach of the frog. This stimulus he believed to be completely annulled by visible radiation, the antagonism being physiological rather than physical. He also stated that exposure of an animal to the mixed radiations of a powerful source of light depresses its heat production, the depression being greater in pigmented animals than in albinos.

No effect on the basal metabolism of healthy men, mice or rats could be observed by Campbell[85] on exposure to a mercury-vapor lamp, or to its rays when filtered through Uviol glass, or to visible light. On the other hand, Sonne[86] found that the oxygen consumption of the chrysalids of the meal worm could be accelerated by light energy of from 1 to 200 gm. cal. per minute per sq. cm. The shorter wave-lengths had the greater effect. There was an increase of about 40 per cent during an exposure of 45 minutes to the unfiltered light of a Kromayer lamp, of about 20 per cent when a glass filter was used and of about 10 per cent when both a glass filter and a methylene blue filter were used. Yellow light had no influence on the respiratory metabolism. An increase of about 15 per cent persisted for several hours after irradiation by unfiltered light, but there were no after effects following irradiation by filtered light which eliminated the central band of ultraviolet frequencies.

Crofts[87] observed a 14-per cent fall in oxygen consumption in canaries on ultraviolet irradiation. This was followed two to six days after the exposure by a rise of 21 per cent. In normal rabbits and in six normal human subjects, no effects were noted which could be ascribed to the irradiation. Lippmann and Völker[88] found a slight increase in human subjects (10 to 18 per cent) but the metabolism returned to normal shortly after the irradiation was discontinued. The administration of iodine did not increase nor prolong the effect. Mělka[89] found a 14- to 47-per cent increase in oxygen consumption in persons exposed to the noon July sun. It has been stated[90] that in certain persons the quartz mercury lamp may produce a fall in total metabolism. This is the effect when the blood bilirubin is high, or if the skin is abundantly pigmented or if there has been an excessive consumption of buckwheat. The effect is ascribed to photosensitization.[91]

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[79] Secerov, S., *Compt. rend.*, **158**, 1826 (1914).

[80] Buschke, A., and Vasarhelyi, J., *Klin. Wochschr.*, **11**, 678 (1932); *Chem. Abs.*, **27**, 779 (1933).

[81] Lenartowicz, J., and Jalowy, B., *Arch. Dermatol. Syphilol.*, **9**, 483 (1938); *Chem. Abs.*, **32**, 9266 (1938).

[82] Schneidewind, A., Albertal, M., and Trajtenberg, S., *Rev. asoc. med. argentina*, **52**, 792 (1938); *Chem. Abs.*, **32**, 9264 (1938).

[83] See, however, Kestner, O., Peemöller, F., and Plaut, R., [*Klin. Wochschr.*, **2**, 2108 (1923)], Kestner, O., Peemöller, F., and Schadow, H., [*Pflüger's Arch. ges. Physiol.*, **217**, 473 (1927)], and Kestner, O., and Schadow, H., [*Ibid.*, **217**, 492 (1927)] for a different point of view.

[84] Harris, D. T., *Proc. Roy. Soc.*, **98B**, 171 (1925).

[85] Campbell, J. A., *Proc. Roy. Soc.*, **99B**, 451 (1926).

[86] Sonne, C., *Acta Radiol. Skand.*, **5**, 419 (1926); *Chem. Abs.*, **21**, 1139 (1927).

Pincussen[92] found solar irradiation to stimulate the protein metabolism of rabbits as shown by an increased nitrogenous excretion. This was still further increased by sensitizers such as dyestuffs and potassium iodide. Liebesny[93] fed two dogs on a constant diet of horse tripe and found exposure to the ultraviolet rays from a mercury-vapor lamp to cause an appreciable reduction in the volume of urine and in the total nitrogen, creatinine, and neutral sulfur content. Yoshine[94] observed a slight rise in the positive nitrogen balance of irradiated dogs if the exposure was short, but this changed to a negative balance when longer exposures were given. Longer periods of irradiation led to disturbances in the absorption of nitrogenous substances in the intestine and to a refusal of food. The slight irradiation which caused the positive balance consisted of a one-hour irradiation on each of eight consecutive days. The severe irradiation consisted of four hours of exposure daily. Fontès and Yovanovitch[95] believed that the exclusion of light decreases the nitrogen metabolism nearly to the level attained during sleep, and that the decrease during sleep while exposed to light is less than that in sleep in darkness. On the other hand, Mayerson, Gunther and Laurens[96] found that in adult dogs transient increases in the endogenous nitrogen metabolism, and in the absorption of calcium and phosphorus from the intestine, resulted when the animals were taken from light to darkness or *vice versa*. It was concluded that any deviation from the usual supply of radiant energy acts as a transient stimulus to these metabolic processes.

Exposure of normal men, women and children to summer sunlight or to a carbon arc causes an increase in creatinine excretion during the period of irradiation, according to Eichelberger,[97] but for a few hours subsequently there is a decreased excretion. No effect was observed on the excretion of creatine or on the basal metabolic rate.

Nothhaas and Schadow[98] studied the nitrogen balance of a series of children, first in Hamburg and again at the sea-shore. In spite of inadequate diet, nitrogen retention is increased under the latter conditions, even although the weight may not be increased. Other children remaining in Hamburg and treated with artificial ultraviolet light showed irregular effects, but in some a positive nitrogen balance was obtained.

[87] Crofts, E., *Am. J. Hygiene*, **8**, 1014, 1024 (1928); *Chem. Abs.*, **23**, 2466 (1929).

[88] Lippmann, A., and Völker, H., *Klin. Wochschr.*, **7**, 213 (1928); *Chem. Abs.*, **22**, 1168 (1928).

[89] Mělka, J., *Bratislava Lekarske Listy*, **6**, 50 (1926); *Chem. Abs.*, **22**, 4137 (1928).

[90] Mason, D. H., and Mason, H. H., *Arch. Int. Med.*, **39**, 317 (1927); *Chem. Abs.*, **21**, 2303 (1927).

[91] Summarizing lectures on the effect of light on metabolism have been given by Pincussen, L., *Strahlentherapie*, **48**, 308 (1933) and by Mangold, E., *Ibid.*, 319.

[92] Pincussen, L., *Biochem. Z.*, **150**, 36 (1924).

[93] Liebesny, P., *Z. Physik. Diatet. Therap.*, **24**, 182 (1920); *Chem. Abs.*, **15**, 2905 (1921).

[94] Yoshine, S., *Strahlentherapie*, **18**, 201 (1924); *Chem. Abs.*, **20**, 1430 (1926).

[95] Fontès, G., and Yovanovitch, A., *Compt. rend. soc. biol.*, **93**, 269 (1925); *Chem. Abs.*, **19**, 3527 (1925).

[96] Mayerson, H. S., Gunther, L., and Laurens, H., *Am. J. Physiol.*, **75**, 399, 421 (1926).

[97] Eichelberger, M., *J. Biol. Chem.*, **69**, 17 (1926).

[98] Nothhaas, R., and Schadow, H., *Jahrb. Kinderheilk.*, **127**, 1 (1930); *Chem. Abs.*, **26**, 763 (1932); see also Ferri, U., *Pediatria Rev.*, **35**, 1110 (1927); *Chem. Abs.*, **22**, 2599 (1928).

Pincussen, Bayerl, Brück, Görne and Rothmann,[99] believed irradiation of pigs with infrared, visible and ultraviolet light to cause, in general, increased elimination of total nitrogen and of purines.

The discrepancies in these reports are due, in part, to the differences in the subjects and the nature and duration of the exposures, and in part to the time following irradiation when the observations were made. It is apparent that no very marked changes occur in most individuals. Lehmann and Szakáll[100] found the effect of ultraviolet irradiation at weekly intervals lowered the basal metabolism of six human subjects 10 to 15 per cent, and increased the capacity for work up to 60 per cent, while decreasing the oxygen debt. The various effects were believed to be very similar to the results attained by training. When an ultraviolet-impervious screen was interposed without the knowledge of the subject, the increased capacity for work did not occur. Another subject showed a loss of weight, a lowering of the basal metabolism and a rise in the respiratory quotient when treated, in contrast to a daily fall in weight and a slight increase in the alkali reserve when not treated.

The pulse rate is usually unaltered, and circulatory effects are not prolonged. The blood pressure is usually lowered, but the circulatory changes are not remarkable. As early as 1905, Hasselbalch[101] observed decreases of from 8 to 10 per cent in blood pressure which lasted for several months following the application of massive doses of the rays from a carbon arc. He ascribed the effects to the cutaneous hyperemia. The most thorough recent studies are by Laurens and Mayerson.[102]

Reed[103] showed that irradiation of the eyes of anesthetized dogs caused a considerable drop in the arterial blood pressure, but there was no evidence for the liberation of a depressor substance into the blood. The effect could not be ascribed solely to nervous factors since it was not abolished by bilateral section of the vagi and section of the optic nerve. The effect was attributed to a direct action upon the blood, since similar effects resulted from the irradiation of the blood circulating through a quartz tube interposed in the carotid artery. The light used was that of a carbon arc and the results were the same when either the infrared rays or the ultraviolet rays of wave-lengths shorter than 3300A had been removed. The coagulation time of the blood was increased, and it was necessary to use intravenous injections of heparin to prevent coagulation of the blood in the circulation. There were no marked effects upon the hemoglobin content or upon the red blood cells, but the white cells decreased, with a relative lymphocytosis and an absolute lymphopenia.[104]

Rowinski[105] could detect no change in the vasoconstricting power of the blood serum of patients who had taken sea or sun baths. Sidoli[106] found that irradiation of the blood serum *in vitro* caused a decrease in its power of vasoconstriction proportional to the intensity of the radiation employed. This he ascribed to a decrease of the adrenalin present in the serum. During irradiation *in vivo*, however, there is no such change.[107]

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[99] Pincussen, L., Bayerl, V., Brück, E., Görne, J., and Rothmann, A., *Strahlentherapie*, **45**, 401 (1932); *Chem. Abs.*, **27**, 4836 (1933).

[100] Lehmann, G., and Szakáll, A., *Arbeits. Physiol.*, **5**, 278 (1932); **6**, 84 (1932); *Chem. Abs.*, **28**, 2396 (1934).

[101] Hasselbalch, K. A., *Skand. Arch. Physiol.*, **17**, 431 (1905); *Berlin Klin. Wochschr.*, **44**, 1247 (1907).

[102] Laurens, H., and Mayerson, H. S., *Am. J. Physiol.*, **84**, 524 (1928).

[103] Reed, C. I., *Am. J. Physiol.*, 74, 511, 518, 525 (1925); bibliography of effect of light on blood pressure is included.

[104] Reed, C. I., *Archiv. Phys. Ther. X-Ray, Radium*, **8**, 108 (1927).

[105] Rowinski, P., *Boll. soc. ital. biol. sper.*, **6**, 818 (1931); *Chem. Abs.*, **26**, 1966 (1932).

[106] Sidoli, E., *Arch. sci. biol. ital.*, **19**, 443 (1934); *Chem. Abs.*, **29**, 3359 (1935).

EFFECTS ON THE BLOOD

The effect of a general irradiation of the body upon the formed elements of the blood is not remarkable, at least in normal individuals. The literature is extensive but frequently contradictory. To summarize the individual papers would leave the reader with a feeling of confusion, and would consume much space. Instead, only a few of the more significant conclusions which it seems possible to draw will be stated, together with references to a few papers from which, as well as from the special works cited earlier in the chapter, the reader may obtain more complete references to other work.[108]

Several writers have found no changes induced in the cell count by irradiation.[109] It seems to be established that normal men or other animals can live on an ample balanced diet for prolonged periods during which sunlight or artificial illumination is absent or much reduced without the production of an anemia.

Hardy[110] tabulated the data of some 45 investigators. Eleven reported no change in the red cells, while 18 reported an increase and only two a decrease. There were wide differences in the species of animal used, and in the conditions of irradiation, sources, energies and wave-lengths. Her own conclusions, after a careful weighing of the available evidence, were that a normal red cell count may be very slightly increased and a low one raised to normal by daily irradiations. Most observers have reported a leucocytosis after ultraviolet irradiation, but there is much variation both in the amount of change in the total white cell count and in the differential count.

One reason for the variations in the results of different observers is that, as pointed out by Balderrey and Barkus,[111] the primary effect of irradiation is a vasodilatation followed by a diffusion of tissue fluid into the blood stream, resulting in dilution and increased blood volume. When the irradiation is long-continued or frequently repeated, this effect may be counteracted by vasoconstriction and blood concentration. Thus, alterations in blood concentration may tend to mask any real variations in the numbers of the various formed elements. At different periods during and after irradiation, these opposing effects may predominate to varying degrees and cause confusion. Mayerson and Laurens[112] found a single exposure to carbon arc radiations to produce a temporary increase in the plasma volume of the blood of dogs, amounting to 6 to 37 per cent, and followed by recovery to normal within five hours. Repeated exposures caused an increase in the number of red cells of 10 to 19 per cent, maintained for three to six weeks after the final irradiations. The color, volume and saturation indexes showed that the cells in the post-irradiation period were usually smaller and less saturated than before irradiation. The platelets dropped in number and volume by 35 per cent during the irradiation, with recovery usually within five hours after each exposure. Leucocytosis resulted from moderate irradiation but markedly low levels in the white blood cell counts followed strong excessive exposures.[113] Excessive irradiation also appeared to destroy red blood cells. In experimental anemias of animals, there seems to be a more rapid restoration of the red cells after ultraviolet irradiation, although too much or too frequent irradiation seems to be definitely harmful.[114] Although the number of red blood cells and the number of reticulocytes increased as a result of irradiation by the flaming carbon arc, the corpuscular volume and the corpuscular hemoglobin did not. In fact, the hemoglobin was practically unaltered. On the other hand, in hemolytic anemia produced by phenylhydrazine, a regeneration of hemoglobin was observed.[115] In nutritional anemias, as the milk anemias, results with the carbon arc were negative, but with the quartz mercury arc, Foster[116] obtained some evidence of a beneficial effect. The number, size, and saturation of the red cells were increased.

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[107] See also Johnson, J. R., Pollock, B. E., Mayerson, H. S., and Laurens, H., *Am. J. Physiol.*, **114**, 594 (1936).

[108] For a review, see Furniss, A., *Brit. J. Actinother.*, **5**, 187 (1930); an alteration in the absorption spectrum of hemolyzed blood was not found following irradiation of the subject by Varshaver, G. S., *Arch. sci. biol. (U S.S.R.)*, **41**, No. 2, 31 (1936); *Chem. Abs.*, **31**, 7905 (1937).

[109] Jaulmes, C., *Compt. rend. soc. biol.*, **92**, 268 (1925); Koopman, J., *Deut med Wochschr.*, **50**, 277 (1924); *Chem. Abs.*, **18**, 2197 (1924); Tataranu, I., *Compt. rend. soc. biol.*, **97**, 1736 (1927); *Chem. Abs.*, **22**, 1799 (1928); Sinclair, R. D., *Sci. Agr.*, **13**, 737 (1933) (in pigs); *Chem. Abs.*, **23**, 3955 (1929).

[110] Hardy, M., *Am. J. Hygiene*, **7**, 811 (1927); **8**, 1024 (1928).

[111] Balderrey, F. C. and Barkus, O., *Am. Rev. Tuberculosis*, **9**, 107 (1924).

[112] Meyerson, H. S., and Laurens, H., *Am. J. Physiol.*, **86**, 1 (1928); *J. Nutrition*, **3**, 465 (1931); *Chem. Abs.*, **25**, 2461 (1931).

Cramer and Drew found light to act as a stimulus to the formation of blood platelets. This has been confirmed by others, including Hardy,[117] Steiner and Gunn,[118] and, in new-born infants, Sanford.[119]

Friedlander and Wiedemer[120] note that in healthy persons the reticulocytes (young red cells) increase in the spring months as contrasted with the count during the winter. They attribute this to an increase in ultraviolet rays from the sun. Seyderhelm,[121] has claimed that dog blood upon ultraviolet irradiation develops the property of causing a sudden outpouring of erythrocytes into the blood of dogs made artificially anemic by saponins. The active substance is associated with the stroma of the irradiated red cells. Normal blood contains small quantities of this active substance. Similar results were obtained in human subjects upon the intramuscular injection of irradiated human cells, the reticulocytosis reaching its maximum one to five hours after the injection. The results in pernicious anemia are not as permanent as those obtained with liver. According to Zaepffel,[122] rapid blood regeneration may be produced in anemic rabbits or patients by the oral administration of solutions obtained by digesting red blood cells with pancreatin followed by exposure to strong ultraviolet light. The final product contained histidine, tryptophane and hematin.

Goldberg[123] found parenteral administration of solutions obtained by irradiating copper or iron plates in water with ultraviolet rays to accelerate the regenerative processes in rabbits made anemic by bleeding. The local anaphylactic reaction is depressed by the use of ultraviolet-treated metals. These materials also produce capillary dilatation in frogs when injected subcutaneously.[124]

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[113] See also Clark, J., *Physiol. Rev.*, **2**, 285 (1922); Koopman, J., *Deut. med. Wochschr*, **50**, 277 (1924).

[114] Hobert, H., *Klin. Wochschr.*, **2**, 1213 (1923); *Chem. Abs.*, **17**, 3893 (1923).

[115] Mayerson, H. S., and Laurens, H., *J. Nutrition*, **4**, 351 (1931); see also Kasatkin, E. V., and Bogdanova, G. P., *Arch. sci. biol. (U.S.S.R.)*, **40**, No. 1, 49 (1936); *Chem. Abs.*, **37**, 6679 (1937).

[116] Foster, P. C., *J. Nutrition*, **4**, 517 (1931); *Chem Abs.*, **26**, 3008 (1932).

[117] Hardy, M., *loc. cit.*

[118] Steiner, P. E., and Gunn, F. D., *Arch. Path.*, **11**, 241 (1931); *Chem. Abs.*, **25**, 4563 (1931).

[119] Sanford, H. N., *Am. J. Diseases Children*, **83**, 50 (1927).

[120] Friedlander, A. and Wiedemer, C., *Arch. Int. Med.*, **44**, 209 (1929).

[121] Seyderhelm, R., *Klin. Wochschr.*, **11**, 628 (1932); *Chem. Abs.*, **26**, 4856 (1932).

[122] Zaepffel, H., *Bull. acad. med.*, **113**, 679 (1935); *Chem. Abs.*, **30**, 7657 (1936).

[123] Goldberg, I. M., *Acta. Med. Skand.*, **85**, 136, 147 (1935); Goldberg, I. M., and Boudyline, V. G., *Ibid.*, 147.

[124] Boudyline, V. G., *Acta. Med. Skand.*, **86**, 88, 95 (1935); see also Griegel, C. R., *Klin. Wochschr.*, **45**, 705 (1936).

Toyoda[125] finds that irradiation of rabbits produces thrombocytogenesis, and a histamine-like substance is believed to be produced in the blood, which acts on the spleen. When the irradiation is repeated more than about five times, thrombopenia results. Such thrombopenic rabbits will again show thrombocytogenesis if a fresh spleen is grafted. When the spleen of a thrombopenic rabbit is grafted to normal splenectomized rabbits, irradiation produces no change in thrombocytes.

According to Tokumitu and Toyota[126] the number of platelets increases in the normal rabbit within an hour after irradiation with rays between 3130 and 3900A, and returns to normal after two to four hours. It does not increase in splenectomized rabbits. In parathyroidectomized rabbits, the increase is more marked than in normal ones. These authors suggest that there exists a specific splenic hormone, which controls thrombocytosis and that its liberation from the spleen is controlled by a histamine-like substance produced in the skin during irradiation. In splenectomized animals the thrombocytosis on irradiation could be observed if normal spleen had been grafted into the animals.

Koh[127] noted that when a rabbit has been irradiated by these wave-lengths for an hour, erythrocytes and hemoglobin are increased in the ear vein within five hours, but they are decreased in the liver and spleen. No reticulocyte increase was noted in any veins. The effect is not due to a regeneration of the corpuscles but rather to an alteration in their distribution. This polyerythemia of the ear veins can be produced in animals from which the thyroid, but not in those from which the spleen, has been removed. It is suggested that the thyroid has a hormone which antagonizes the splenic hormone and that the former is concerned with the redistribution of erythrocytes after the irradiation. Carnielli reports that irradiation of rats and guinea pigs produces a considerable increase of the oxidase in the leucocytes.[128]

Recently there have been many determinations of the ultraviolet absorption of blood, its plasma and serum, and attempts have been made to correlate variations in the absorption spectra with diseased conditions. These are not discussed, since they have not as yet led to any very useful results and because our subject matter is limited to effects dependent upon the occurrence of photochemical processes.

Macht and Blackman[129] noted that animals poisoned with carbon monoxide and exposed to ultraviolet rays recovered more quickly than controls poisoned to the same degree and kept in darkness. This was attributed to the photodissociation of the carbon monoxide-hemoglobin. Estler,[130] however, was unable to verify these observations and concluded that the *in vitro* dissociation of the complex with hemoglobin had no counterpart *in vivo*. Gorkin finds the dissociation can be affected by daylight, but not by ultraviolet light.[131]

Harris[132] finds that irradiation of blood causes it to give up oxygen at high oxygen tensions and to take it up at low tensions. Both effects are irreversible in darkness. At about 15 mm. tension of oxygen there is gaseous equilibrium. The taking up of the oxygen by blood in ultraviolet light he believed to be a property of the plasma. In the presence of traces of certain sensitizing substances, iron chloride, dyes, and especially hematoporphyrin and chlorophyll, the velocity of the photoöxidation of plasma may be increased up to a hundred fold. The accelerating effect of hematoporphyrin is unaffected by the addition of sodium cyanide. It was noted in Chapter 34 that certain proteins and the aromatic amino- acids undergo a similar photoöxidation. Krebs[133] finds that light affects the hemin catalysis of the oxidation of cysteine to cystine by molecular oxygen in the same way that it affects the respiration of living systems.

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[125] Toyoda, G., *J. Chosen Med. Assoc.*, **22**, 673 (1932); **26**, 856, 1017 (1936); *Chem. Abs.*, **31**, 1869 (1937).

[126] Tokumitu, Y., and Toyota, G., *Trans. Japan. Path. Soc.*, **21**, 191 (1931); *Chem. Abs.*, **26**, 6003 (1932).

[127] Koh, M., *J. Chosen Med. Assoc.*, **22**, 775 (1932); *Chem. Abs.*, **27**, 2197 (1933).

[128] Carnielli, P., *Biochem. terap. sper.*, **25**, 1 (1938); *Chem. Abs.*, **32**, 4183 (1938).

[129] Macht, D. I., and Blackman, S. S., Jr., *J. Pharmacol.*, **23**, Proc. 142 (1924); *Chem. Abs.*, **18**, 3228 (1924).

[130] Estler, W., *Arch. Hyg. Bakt.*, **115**, 152 (1936); *Chem. Abs.*, **30**, 3096 (1936).

[131] Gorkin, Z. D., *J. Physiol (U.S.S.R.)*, **22**, 329 (1937); *Chem. Abs.*, **32**, 9103 (1938).

[132] Harris, D. T., *Biochem. J.*, **20**, 280, 271 (1926).

[133] Krebs, H. A., *Biochem. Z.*, **193**, 347 (1928).

The oxygen consumption of red blood cells (and also of yeast cells) in Tyrode's solution at pH 7.2 may be increased by 50 per cent during irradiation by ultraviolet light, according to Surányi and Vermes.[134] Cyanide irreversibly inhibits both the normal and the increased respiration.

Hemolysis. Suspensions of red blood cells are slowly hemolyzed by visible light.[135] Meyerstein[136] found human cells which in physiological salt solution were hemolyzed in 13 to 14 days in darkness, hemolyzed in 5 to 6 days in light. Radiations of wave-lengths less than 2700A are more effective, according to Koeppe.[137] Hausmann and Sonne[138] found it possible to sensitize the cells to the longer wave-lengths of the ultraviolet by means of hematoporphyrin. The effect is then most marked at 3130A. *In vivo* this effect could not be demonstrated. Löhner[139] found arsenious acid to sensitize red blood cells to either visible or ultraviolet light. Fabre and Simonnet[140] state that cholesterol-free lecithin, if irradiated in the presence of hematoporphyrin by ultraviolet light, undergoes a change by which it acquires a greater hemolytic power than it can attain on unsensitized irradiation.

During the irradiation of normal persons a gain in fecal urobilin was observed by Teplov and Mesheristkaya.[141] This was attributed to increased hemolysis. At the same time the production of red cells was stimulated, so that the total number of red cells and the hemoglobin content of the blood usually remained constant. In anemic subjects, the apparent regeneration of the blood is explained by an overcompensation which causes the rate of the production of blood to exceed the rate of hemolysis. At the conclusion of the treatment, the rate of hemolysis sinks rapidly to normal, and the overproduction of red cells also subsides.

Farkas and Tangl[142] had noted, on the contrary, that in dogs, unless splenectomized, ultraviolet irradiation inhibits the passing out of their blood pigment.

Ward[143] has claimed that the influenza bacillus when grown on blood-agar plates is unable to produce hemolysis if incubated in darkness. If it is then exposed to sunlight or artificial light, it shows a definite hemolysis after a time which depends upon the intensity of the light.

The permeability of erythrocytes to water-soluble substances, such as glycerol, glucose, etc., is said to be increased by light.[144] The spectral distribution of the efficiency of radiation in decreasing the stability of the red cells corresponds very closely to that of the absorption of radiations by oxyhemoglobin.[145] This suggests that the effect is exerted upon the hemoglobin rather than upon the colorless cell membrane.

Although hematin and hemochromogen are not altered by sulfur dioxide in darkness, when illuminated with this compound they lose iron and are converted into hematoporphyrin-like substances. These differ from Nencki's hematoporphyrin in their sulfur content and in their solubility, according to Zeynek and Kittel.[146] Under similar conditions, blood pigments also lose their iron and are converted into porphyrin-proteoses, containing varying amounts of more or less firmly bound proteins. Light sensitization of white mice by these products differs little from sensitization by Nencki's hematoporphyrin.

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[134] Surányi, G., and Vermes, M., *Magyar Orvosi Arch.*, **30**, 585 (1929); *Chem. Abs.*, **25**, 2162 (1931).

[135] Hausmann, W., and Loewy, A., *Biochem. Z.*, **173**, 1 (1926); Earle, W. R., *J. Exptl. Med.*, **48**, 457, 667, 583 (1928); Lepeschkin, W. W., *Science*, 73, 568 (1931).

[136] Meyerstein, *Klin. Wochschr.*, **7**, 2244 (1928); *Chem. Abs.*, **23**, 1438 (1929).

[137] Koeppe, H., *Arch. Kinderheilk.*, **79**, 109, 198 (1926).

[138] Hausmann, W., and Sonne, C., *Strahlentherapie*, **25**, 174 (1927).

[139] Löhner, L., *Biochem. Z.*, **186**, 194 (1927).

[140] Fabre, R., and Simonnet, H., *Compt. rend.*, **184**, 707 (1927).

[141] Teplov, I., and Mesheristkaya, R., *Deut. Arch. Klin. Med.*, **174**, 399 (1933); *Chem. Abs.*, **27**, 5347 (1933).

[142] Farkas, G., and Tangl, H., *Biochem. Z.*, **200**, 184 (1928); *Chem. Abs.*, **23**, 168 (1929).

[143] Ward, H. K., *J. Bacteriol.*, **15**, 51 (1928).

[144] Lepeschkin, W. W., *Protoplasma*, **18**, 243 (1933); *Chem. Abs.*, **27**, 3228 (1933).

[145] Lepeschkin, W. W., and Davis, G. E., *Protoplasma*, **20**, 188 (1933); *Chem. Abs.*, **28**, 1722 (1934).

Vital staining in the red cells of frogs is said to be materially retarded by light rays of the shorter wave-length half of the visible spectrum.[147]

Falk and Reed[148] found that in blood directly irradiated *in vivo*, there is a small but definite decrease in the negative electrophoretic potential of the red cells.

Blood Sugar and Carbohydrate Metabolism. Frenkel-Tissot[149] believed, as a result of studies at high altitudes, that people with high blood sugar tend to have this decreased by irradiation by the sun or the mercury arc or by hyperthermia, although those with normal or low blood sugar values show a tendency for the sugar to be increased by the same treatments. Many subsequent observers have noted a depression of the blood sugar on irradiation.[150] Petersen and v. Oettingen[151] found that in dogs a short exposure was as effective as a longer one in causing a reduction in the amounts of sugar and chlorides in the lymph, an increase in the number of white cells in the blood, and in the volume and protein content of the lymph.

When blood is directly irradiated in quartz tubes *in vivo* by the method of Reed, in anesthetized dogs, the blood sugar is not affected.[152] Treatment of guinea pigs, cats and dogs with serum which had been previously irradiated in most cases reduced the elimination of sugar by the liver.[153]

Keeser[154] observed that rabbits placed in blue light and injected intravenously with glucose show a less pronounced and shorter hyperglucemia than those injected in daylight. Irradiation also causes an increased content of sugar in the skin. There is also a marked decrease of from 31 to 15 mg. per cent in the reduced glutathione content of the skin and a smaller decrease in that of the blood. Keeser[155] believes blue light to have a sympathicotonic and red light a vagotonic action.

Ogawa[156] found the reduced glutathione in both arterial and venous blood of irradiated rabbits to be decreased immediately after irradiation. After thirty to sixty minutes, however, it increased markedly. The same was true of the content of the oxidized form in arterial blood, but in the venous blood it increased immediately after the irradiation.

[146] Zeynek, R., and Kittel, S., *Z. physiol. Chem.*, **224**, 233 (1934); *Chem. Abs.*, **28**, 4079 (1934).

[147] Kedrovskil, B., *Protoplasma*, **22**, 607 (1935); *Chem. Abs.*, **29**, 3362 (1935).

[148] Falk, I. S., and Reed, C. I., *Am. J. Physiol.*, **75**, 616 (1926).

[149] Frenkel-Tissot, H. C., *Deut. Arch. Klin. Med.*, **133**, 286 (1920); *Chem. Abs.*, **15**, 118 (1921).

[150] Pincussen, L., and Jacoby, D., *Biochem. Z.*, **195**, 449 (1928); Bloch, C. E., and Faber F., *Am J. Dis. Children*, **30**, 504 (1925); Rothmann, H., *Klin. Wochschr.*, **2**, 881 (1923); Pincussen, L., and Yakota, S., *Biochem., Z.*, **241**, 398 (1931); Pincussen, L., *Biochem, Z.*, **272**, 354 (1934); *Klin. Wochschr.*, **10**, 791 (1933); **11**, 1231 (1932); *Chem. Abs.*, **26**, 5612 (1932); *Strahlentherapie*, **51**, 537 (1934).

[151] Petersen, W. F., and v. Oettingen, W. F., *Arch. Exptl. Path. Pharmakol.*, **123**, 160 (1927); *Chem. Abs.*, **22**, 276 (1928).

[152] Reed, C. I., Payte, J. I., and Lackey, R. W., *Proc. Soc. Exptl. Biol. Med.*, **24**, 11 (1926).

[153] Holtz, P., *Arch. Ges. Physiol. (Pflüger's)*, **226**, 578 (1931); *Chem. Abs.*, **25**, 2194 (1931).

[154] Keeser, E., *Arch. Expt. Path. Pharmakol.*, **166**, 624 (1932) .

[155] See also von Deschwander, J., who attributes the results to increased insulin formation; [*Strahlentherapie*, **39**, 278 (1931); *Chem. Abs.*, **25**, 1886 (1931); *Strahlentherapie* **46**, 713 (1933); *Chem. Abs.*, **27**, 3489 (1933)].

[156] Ogawa, M., *J. Agr. Chem. Soc. Japan*, **13**, 81 (1937); *Chem. Abs.*, **31**, 3077 (1937).

Jona[157] gave progressively increasing daily irradiations to four normal persons and two diabetics for a month. In the normal persons there was a diminution in glucemia but no notable effect on the glucose tolerance or glycosuria. In the diabetics it was found that although both the glucemia and glycosuria were diminished, the general condition of the patients was adversely affected and the acetonuria increased.

Gorini[158] finds that small doses of ultraviolet rays enhance the glucose metabolism and large doses depress it. In infants and children, the blood sugar is increased by ten minutes and reduced by twenty minutes of irradiation or by the use of greater intensities, according to Ferri.[159] In alimentary hyperglucemia, the reaction is hastened by short and retarded by long exposures, but adrenalin hyperglucemia is always enhanced by irradiation. Ceruti[160] determined the glucemic titer before and after the irradiation of albino rats. In a group exposed to the direct rays of the mercury-vapor lamp for 15, 30 and 60 minutes, there was an average diminution of 10, 25 and 31 per cent respectively. In a group exposed with a Wood glass filter the values were 8, 13, and 18 per cent, and in a third group in direct sunlight, 6, 9 and 12 per cent.

Kallós and Kallós-Deffner[161] found that ultraviolet light lowered the fasting blood sugar and increased the sugar tolerance of rabbits which had been previously kept in darkness for a week.[162] On the other hand, Müller[163] found no difference in the blood sugar level of rabbits kept in darkness for two or three weeks from that of those kept in the light. Nor could a difference in the glucose tolerance be detected.

Ventral irradiation is said to be more effective than dorsal in producing a constant and progressive decrease in the blood sugar of rabbits by Benvenuto,[164] who did not succeed, however, in demonstrating an effect upon the glucose tolerance. Besides noting a decrease in the blood sugar which reaches its maximum at the height of the erythema, Marchionini and Hövelborn[165] found the blood diastase to be increased by ultraviolet irradiation.

Burge and Wickwire[166] find that the normal rate of utilization of glucose and galactose by *Paramecium caudatum* is depressed by ultraviolet irradiation. This effect is abolished by the addition of insulin to the medium and was thought to be due to the destruction of insulin in the living cells by the irradiation.

Pincussen and Jacoby[167] find the lactic acid content of the whole blood of rabbits to decrease by 20 to 30 per cent shortly after an irradiation. The content in the serum, however, increases. The authors suggest that during irradiation the permeability of the corpuscles may increase so as to permit the passage of a considerable part of their lactic acid into the serum. The glycogen of heart and muscle, if changed at all, decreases slightly, although the total carbohydrate increases considerably. It appears therefore, that irradiation causes a sparing of sugar but it was uncertain whether this was due to a decreased breakdown of the sugar or to an increased formation of sugar from lactic acid. Later, however, Pincussen and Kawakami[168] stated that in the liver and muscles of irradiated animals there is an increase in glycogen at the expense of lactic acid. The glycocen: lactic acid ratio is raised 55 and 45 per cent in the liver and muscles, respectively, but in the heart the change does not exceed the experimental error. They believe the radiations to act in a manner similar to that of insulin.

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[157] Jona, A., *Minerva Med.*, **II**, 757 (1933), *Chem. Abs.*, **28**, 1401 (1934).

[158] Gorini, P., *Pediatria Rivista*, **35**, 1110 (1927); *Chem. Abs.*, **22**, 2599 (1928).

[159] Ferri, U., *Riv. clin. pediatr.*, **25**, 217 (1927); *Chem. Abs.*, **22**, 619 (1928).

[160] Ceruti, G., *Boll. soc. ital. biol. sper.*, **3**, 30 (1928); *Chem. Abs.*, **22**, 2383 (1928).

[161] Kallós, P., and Kallós-Deffner, L., *Strahlentherapie*, **50**, 191 (1934); *Chem. Abs.*, **28**, 4772 (1934). See also Root, R. W., *Arch. Phys. Therapy, X-Rays, Radium*, **12**, 153 (1931); *Chem. Abs.*, **26**, 1648 (1932).

[162] See also Rothman, S., *Strahlentherapie*, **51**, 364 (1934); Pincussen, L., *Ibid.*, **53**, 7 (1934).

[163] Müller, R. W. J., *Biochem. Z.*, **276**, 416 (1935).

[164] Benvenuto, E., *Pediatria Riv.*, **43**, 675 (1935), *Chem. Abs.*, **30**, 4182 (1936).

[165] Marchionini, A., and Hövelborn, C., *Klin. Wochschr.*, **14**, 1387 (1935); *Chem. Abs.*, **30**, 2997 (1936).

[166] Burge, W. E., and Wickwire, G. C., *J. Biol. Chem.*, **72**, 827 (1927).

[167] Pincussen, L., and Jacoby, D., *Biochem. Z.*, **195**, 449 (1928).

By irradiating muscle extract before incubation, Stiven[169] has found it possible to increase the rate of lactic acid formation from glycogen. In one case the rate of lactic acid formation in the irradiated sample was three times that in the control. Irradiation leads also to alterations of the accumulation of the phosphoric ester. Brief irradiations resulted in an increase of the ester accumulation, but longer ones produced a decrease. The higher rates of lactic acid formation coincide with a decrease in the ester accumulation. In only one of thirteen experiments was the lactic acid formation decreased after a long irradiation, and in this case the accumulation of ester was almost completely inhibited.

Blood pH. During the first hour after irradiation, there is a transient blood acidosis in human subjects, according to Kroetz.[170] This amounts to a drop of about 0.3 to 0.7 in pH and is ascribed by Kroetz to introduction into the blood of the altered proteins or their disintegration products formed as a result of the irradiation. This phase is followed by a more permanent alkalosis reached about 24 hours after the exposure. In it, the blood pH is raised about 0.05 to 0.07 unit above normal. This is ascribed to shifts of bases from the tissues to the blood. During the stage of acidosis, the blood is hydrated, but in the later stages the serum becomes more concentrated. In the early acidosis, the respiratory center is stimulated and there may be some hyperventilation. The alteration of the ionic equilibrium in the serum of the irradiated individual is summarized as an increase in the ratio $K^+ \times (H_2PO_4' + HPO_4'')/Ca^{++}$. Refractometric measurements revealed an alteration in the nature of the serum proteins. The early increase in blood acidity was also obtained as a result of the *in vitro* irradiation of blood. Hoeber[171] found ultraviolet light to render horse serum more acid. On the other hand, Moran and Reed[172] found irradiation of dog blood *in vivo* to fail to produce any constant effect on the carbon dioxide combining power.

According to Balderrey and Barkus[173] exposure of the human body to sunlight increases the alkalinity of the blood. The amount of pigmentation present has a direct influence on the change of the blood reaction, the greater the amount of pigmentation the more marked being the change in the blood pH. In their experiments, the effects were probably to be attributed predominantly to radiations of the visible spectrum. Variations in the intensity of the light materially influenced its effects on the blood reaction.

In earlier studies, Ederer[174] determined the influence of the light of a quartz lamp upon the alveolar carbon dioxide tension of man. The results varied with the dosage administered. Weak stimulation had no effect. Radiations of medium intensity increased the carbon dioxide tension but strong irradiation lowered it. The effects appeared to be independent of the skin erythema. The hypercapnic effect was considered to be hematogenous and not of central origin. This interpretation was based upon a belief, then undemonstrated, in a probable increase in the alkalinity of the blood, a decrease in the acid products of metabolism and a change in the colloidal state of the blood proteins.

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[168] Pincussen, L., and Kawakami, T., *Biochem Z.*, **208**, 185 (1929); Pincussen, L., *Arch. Phys. Therapy, X-Ray, Radium*, **18**, 750 (1937); *Chem. Abs.*, **32**, 4615 (1938).

[169] Stiven, D., *Biochem. J.*, **24**, 172 (1930).

[170] Kroetz, C., *Biochem. Z.*, **151**, 146, 449 (1924).

[171] Hoeber, R., *I a Med. Germano-Hispano Amer*, **1**, 113 (1923); *Physiol. Abs.*, **10**, 61; *Chem. Abs.*, **19**, 3115 (1925); see also Frontali, G., *Rev. Clin. Pediatr.*, **25**, 661 (1927); *Chem. Abs*, **23**, 1657 (1929). There is a slight decrease in total nitrogen and albumin nitrogen and an increase in the globulin nitrogen, according to Murayama, M., *J. Oriental Med.*, **34**, 79 (1936); *Chem. Abs.*, **31**, 5820 (1937).

[172] Moran, W. H., and Reed, C. I., *Proc Soc. Exptl. Biol. Med.*, **24**, 179 (1926).

[173] Balderrey, F. C., and Barkus, O., *Am. Rev. Tuberculosis*, **9**, 107 (1924).

[174] Ederer, S., *Biochem. Z.*, **132**, 103 (1922); *Chem. Abs.*, **17**, 303 (1923).

Glass[175] observed for two to four hours after intense ultraviolet treatment, a change in the chlorine distribution in the blood, which was regarded as an indication of a shift in the acid-base equilibrium in the blood toward an acidotic condition. This sometimes persisted for 24 hours.

The analysis of urine samples during an hour after a single irradiation failed to indicate to Essinger and György[176] any shift in the acid-base equilibrium. The serum calcium was slightly decreased.

Iancou and Iana[177] determined the pH of the blood serum of eleven nursing mothers at the beginning, middle and end of a period of irradiation of the mammary glands. In seven, it rose appreciably, in one it remained constant, in two it at first dropped slightly and then returned to its initial value and in one suffering from an infection it dropped very slightly. In six cases the calcium content rose appreciably and in the other five it dropped slightly. The action on the nurslings was even less pronounced, unstable and inconstant. Lenzi[178] believes irradiation to cause no change in the blood pH.

The effects of general body irradiation upon other features of the blood composition have been frequently studied. In normal subjects, no very pronounced changes in phosphorus in its various forms, chlorine, magnesium, calcium, sodium or potassium have been found. Slight positive or negative variations may be produced at various periods during or after irradiation, but rarely have marked changes been observed.[179]

Frontali[180] noted an increase in the inorganic phosphorus of serum which had been irradiated fifteen to sixty minutes by a mercury arc. Sacchi[181] observed a decrease in the phosphatase content of the bones of rats kept in darkness, which could be restored to normal by exposing them to direct sunlight for a week.

In the *in vivo* irradiation of blood streaming through a quartz tube interposed in the circulation, Reed and Tweedy[182] found no immediate changes in the blood calcium. No effects upon the diffusibility of the serum calcium could be observed to follow either the irradiation of an animal or of its serum directly, by Moritz.[183] The addition of calcium chloride to rabbit serum, previously irradiated either *in vivo* or *in vitro*, is said to depress its electrical conductivity; the effect is not observed in the absence of the preceding irradiation.[184]

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[175] Glass, J., *Biochem. Z.*, **231**, 45 (1931); *Chem. Abs.*, **25**, 2160 (1931).

[176] Essinger, R., and György, P., *Biochem. Z.*, **149**, 344 (1924).

[177] Iancou, A., and Iana, I., *Bull. soc. péd.*, **30**, 76 (1932); *Chem. Abs.*, **27**, 3729 (1933).

[178] Lenzi, F., *Biochim. terap. sper.*, **23**, 118 (1936); *Chem. Abs.*, **30**, 6018, 6772 (1936).

[179] Lodenkämper, H. *Balneologie*, **1**, 438 (1934); *Chem. Abs.*, **31**, 3948 (1937); Kroetz, C., *Biochem. Z.*, **151**, 449 (1924); Malczynski, S., *Compt. rend. soc. biol.*, **113**, 1297 (1923); *Chem. Abs.*, **27**, 5345 (1933); Pincussen, L., and Makrineos, I., *Biochem. Z.*, **161**, 61, 67 (1925); Mayerson, H. S., Gunther, L., and Laurens, H., *Proc. Soc. Exptl. Biol. Med.*, **22**, 469 (1925); Bomskov, C., and von Rose, M., *Klin. Wochschr.*, **10**, 1956 (1931); *Chem. Abs.*, **26**, 2495 (1932); Malczynski, S., Borsiewicz, A., and Toczyski, T., *Compt. rend. soc. biol*, **108**, 165 (1931); *Chem. Abs.*, **26**, 2754 (1932); von Rose, M., *Z. Kinderheilk*, **54**, 236 (1933); *Chem. Abs.*, **27**, 2985 (1933); Egidi, E., and Rowinski, P., *Boll. soc. ital. biol. sper.*, **9**, 118 (1934); *Chem. Abs.*, **28**, 3746 (1934); Stiemens, H., and Heringa, G., *Nederland. Tijdschr. Geneeskund.*, **77**, **II**, 1635 (1933); *Chem. Abs.*, **28**, 2732 (1934); Brown, W. H., and Howard, M., *J. Exptl. Med.*, **49**, 103 (1929); Fairhall, L. T., *Am. J. Physiol.*, **84**, 378 (1928); Maynard, L. A., Goldberg, S. A., and Miller, R. C., *Proc. Soc. Exptl. Biol. Med.*, **22**, 494 (1925); Orr, J. B., Magee, H. E., and Henderson, J. M., *J. Physiol*, **70**, *Proc.* 25 (1924); Howe, M. G., and Medlar, E. M., *Am. Rev. Tuberculosis*, **10**, 408 (1924); Moritz, A. R., *J. Biol. Chem.*, **64**, 81 (1925); Cheymol, J., and Quinquaud, A., *J. pharm. chim.*, **16**, 233 (1932); *Chem. Abs.*, **27**, 1901 (1933); Pincussen, L., *Biochem. Z.*, **182**, 359 (1927).

[180] Frontali, G., *Riv. Clin. Pediatra*, **25**, 661 (1927); *Chem. Abs.*, **23**, 1657 (1929); also De Toni, G., and Stancati, A., *Boll. soc. ital. biol. sper.*, **4**, 165 (1929); *Chem Abs.*, **23**, 3721 (1929); Careddu, G., *Biochim. terap. sper.*, **18**, 109 (1931); *Chem. Abs.*, **25**, 4015 (1931).

[181] Sacchi, U., *Boll. soc. ital. biol. sper.*, **9**, 94 (1935); *Chem. Abs.*, **29**, 4781 (1935).

[182] Reed, C. I., and Tweedy, W. R., *Am. J. Physiol.*, **76**, 54 (1926).

In marked contrast to the observations upon normal subjects are the results obtained in rachitic animals discussed in Chapter 38. The irradiation of normal rabbits was found by Grant and Gates[185] to cause an hypertrophy of the parathyroids. Nonidez and Goodale[186] found that when young chicks were kept on a ration poor in vitamin C and deprived of direct sunlight, an enlargement of the parathyroid gland resulted. It was due to an increase in the size and number of epithelial cells. This was followed by a phase of regression and in some cases by local degenerative changes. Subsequent exposure to sunlight led to a decrease of the gland volume with a considerable crowding of the epithelial cells and sometimes to pressure atrophy.

The irradiation of parathyroidectomized dogs did not significantly increase their blood calcium level, according to Swingle and Rhinhold.[187] Jung[188] however, found daily doses of ultraviolet light fifty times those commonly applied to unhabituated human subjects, to benefit parathyroidectomized white rats. He believed the parathyroid to have some function related to the photochemistry of the skin. Drucker and Faber[189] found that irradiation during tetany brought the calcium to a normal level without changing the blood pH or affecting the antagonistic relation between phosphorus and calcium. The increase in total serum calcium does not occur immediately following the irradiation of children with tetany as is the case with inorganic phosphorus. Indeed, it comes subsequent to the effects on the tetany. Calcium in the ultrafiltrate is generally below 50 per cent of the total calcium before irradiation. It increases in successive determinations and comes to exceed 60 per cent of the total calcium. Later a gradual increase in total calcium ensues.[190]

Although Malczynski[191] found a considerable increase in the blood cholesterol of irradiated human subjects, Ornstein found no significant changes.[192] Pincussen and Zuckerstein[193] found the serum cholesterol unchanged in irradiated animals, although the total ether extract of the serum was definitely increased. In rabbits, Kultjugin[194] found irradiation to increase the cholesterol not over 30 per cent, although the blood fat was greatly increased after the second exposure.

Hubert[195] believes that patients with carcinoma usually show a decrease in the serum cholesterol after irradiation. There are, however, so many exceptions that it is unlikely that this response to irradiation can have diagnostic significance.

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[183] Moritz, A. R., *J. Biol. Chem.*, **64**, 81 (1925).

[184] Dell Aquila, A., and Jaia, F., *Arch. farmacol. sper.*, **60**, 578 (1935); *Chem. Abs.*, **30**, 4520 (1936).

[185] Grant, J. H. B., and Gates, F. L., *Proc. Soc. Exptl. Biol. Med.*, **21**, 230 (1924); *J. Exptl. Med.*, **45**, 115 (1927).

[186] Nonidez, J. F., and Goodale, H. D., *Am. J. Anatomy*, **38**, 319 (1927); *Chem. Abs.*, **21**, 2016 (1927).

[187] Swingle, W. W., and Rhinhold, J. S., *Am. J. Physiol.*, **75**, 59 (1925).

[188] Jung, F. T., *Endocrinology*, **12**, 81 (1928); *Chem. Abs.*, **22**, 2575 (1928); see also Vines, H., *Endocrinology*, **11**, 125 (1927); *Chem. Abs.*, **21**, 3960 (1927).

[189] Drucker, P., and Faber, F., *J. Biol. Chem.*, **68**, 57 (1926).

[190] Careddu, G., *Atti soc. med. Padova*, **15**, 126 (1937); *Chem. Abs.*, **32**, 6273 (1938).

[191] Malczynski, S., *Compt. rend. soc. biol.*, **99**, 922 (1928); *Chem. Abs.*, **23**, 401 (1929).

[192] Ornstein, T., *Compt. rend. soc. biol.*, **103**, 190 (1930); *Chem. Abs.*, **25**, 117 (1931).

[193] Pincussen, L., and Zuckerstein, E., *Biochem. Z.*, **207**, 426 (1929).

[194] Kultjugin, A., *Biochem. Z.*, **186**, 36 (1927).

[195] Hubert, R., *Arch. Gynäkol.*, **146**, 51 (1931); *Chem. Abs.*, **25**, 5926 (1931); *Arch. Gynäkol.*, **149**, 433 (1932); **151**, 681 (1932); *Chem. Abs.*, **27**, 2462 (1933).

The total blood sulfur is said to be lowered after ten minutes of irradiation.[196] Free sulfur and oxidized sulfur diminished in a parallel manner, but the former much more rapidly than the latter, so that the ratio of oxidized sulfur to total sulfur was, in general, increased.[197]

In vitro irradiation of human blood serum lowers its surface tension, although the results of *in vivo* irradiation are uncertain.[198] The index of refraction of normal horse serum at 20°C. increased progressively from 1.3466 to 1.3531 during thirty minutes of irradiation. Beef plasma showed a similar behavior and there were similar increases in antitetanic, antistreptococcic and antidiphtheric sera.[199] The change is attributed to an alteration of the state of the proteins.

The gelatinization of serum is said to be accelerated by ultraviolet rays.[200]

An acceleration of the rate of red cell sedimentation is produced over only a limited range of dosages, beyond which the rate tends to be retarded.[201]

The blood and skin of rabbits which have been irradiated over a period of three to six weeks is found by Engel [202] to contain a substance which induces cornification in castrated female mice. Its formation is not promoted by the simultaneous injection of cholesterol. Ultraviolet irradiation of castrated female rats and mice does not produce a positive Allen-Doisy test.

Blood Enzymes. Pincussen [203] found the activity of the blood catalase of rabbits kept in darkness slightly greater than that of animals exposed to ultraviolet light, especially if they had been given a sensitizer. In rats, the diminution is especially marked in the liver.[204] Koldayev and Altschuller [205] noted a transitory decrease in the serum amylase and blood catalase of irradiated rabbits. Castagna [206] found the longer rays of sunlight to increase the blood catalase of mice over that in those kept in darkness, these having almost none. Irradiation in the wavelength range 3190 to 3900A did not materially change the catalase content. When both this radiation and visible light were used, the catalase content increased during the first three hours of irradiation and then declined. Daily sunbaths are said to cause a small increase in human blood catalase.[207]

The general irradiation of rabbits produces a proteinase capable of attacking skin and serum proteins, according to Abderhalden and Tetzner.[208] Schamberg and Brown [209] find that exposure of rabbits to ultraviolet light decreases the concentration of lipase and increases that of proteinase in the blood. In the skin, both are decreased. Vedder [210] observed that when leucocytes are irradiated with visible light, the granules which contain oxidase disappear only if the temperature is raised above 62°. Ultraviolet irradiation, however, is effective at ordinary temperatures.

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[196] Loeper, M., Degos, R., and Lesure, A., *Compt. rend. soc. biol.*, **106**, 718 (1931); *Chem. Abs.*, **25**, 3370 (1931).

[197] See also Loeper, M., Decourt, J., Olivier, J., Tonnet, J., and Lesure, A., *Compt. rend. soc. biol.*, (1926-7).

[198] Gobel, *Biochem Z.*, **190**, 95 (1927); Tamura, A., *Acta Schol Med. Univ. Kyoto*, **16**, 253 (1934); *Chem. Abs.*, **28**, 4754 (1934).

[199] Cluzet, J., and Kofman, T., *Compt. rend. soc. biol.*, **98**, 978 (1928); *Chem Abs.*, **22**, 3179 (1928).

[200] Kopaczewski, W., *Compt. rend.*, **198**, 1947 (1934).

[201] Kostyal, L., *Biochem. Z.*, **299**, 100 (1930).

[202] Engel, P., *Endokrinologie*, **20**, 86 (1938); *Chem. Abs.*, **32**, 8452 (1938).

[203] Pincussen, L., *Biochem. Z.*, **168**, 474 (1926).

[204] Pincussen, L., and Tanino, F., *Biochem Z.*, **234**, 478 (1931).

[205] Koldayev, B., and Altschuller, M. M., *Z. physiol. Chem.*, **186**, 223 (1930).

[206] Castagna, S., *Biochim terap. sper*, **13**, 48 (1926); *Chem. Abs.*, **20**, 2529 (1926); *Arch. sci. biol. ital.*, **10**, 118 (1927); *Chem. Abs.*, **22**, 97 (1928).

[207] Deribas, D., and Kornmann, J., *Bull. soc. chim. biol.*, **18**, 418 (1936), *Chem. Abs.*, **30**, 5244 (1936).

[208] Abderhalden, E., and Tetzner, E., *Fermentforschung*, **14**, 522 (1935); *Chem. Abs.*, **29**, 8010 (1935).

[209] Schamberg, J. F., and Brown, H., *Arch. Int. Med.*, **35**, 537 (1925).

[210] Vedder, A., *Nederland. Tijdschr. Geneeskunde*, **68**, 2357 (1924); *Chem. Abs.*, **19**, 1143 (1924).

Effects on Immune Bodies in Blood. In general, irradiation does not affect the bactericidal properties of the blood of an irradiated subject.[211] After long periods of intense ultraviolet irradiation of rabbits, Albela [212] found no alteration of the phagocytic action of the blood serum, as determined by the concentration of opsonins. Koopman [213] observed that although the complement of the blood of a guinea pig was almost doubled during the first hour of irradiation of the animal, its concentration decreased markedly during a further two hours of exposure. This usually produced death and the blood was found free from complement. Gordon and Wormall [214] did not find the irradiation of guinea pigs to increase the serum complement. Osborn [215] found an occasional increase in the case of young, weaned rats, but this could not be uniformly obtained. Mesik reports a sharp drop during the irradiation, with a return to normal upon its cessation.[216]

Matushita [217] found irradiation of the skin of rabbits with ultraviolet rays to increase the amount of antityphoid substance in the serum (confirmed by Mesik), an effect especially marked in the serum of immunized animals. Both the skin and the spleen were necessary for irradiation to evoke this response. Irradiation of the skin was believed to produce a histamine-like substance which causes the spleen to release a hormone that controls the production of the antityphoid substance. Bessemans and Seldeslacht [218] found that rabbits injected with an emulsion of typhoid bacilli and then treated with ultraviolet rays showed a larger production of antibodies than non-irradiated animals.

Heuer and Potthoff [219] found that an exposure of animals to ultraviolet rays had only a slight influence on the formation of antibodies. Pigmented animals show this influence more than unpigmented ones. However, at the height of antibody formation, when the titer is somewhat constant, exposure of animals to ultraviolet rays causes a very great increase in the titer. This effect is not permanent and the return of the titer to the preimmunization level is much more rapid than in nonexposed animals. Wenger [220] finds carbon-arc irradiation of a small area on the back of a pig sufficient to produce a slight erythema to cause a moderate increase in the bactericidal action of the blood. This effect is considerable, he believes, when the erythema is severe.

Abe finds that irradiation of black rabbits accelerates the production of the agglutinin for *B. coli*, more marked than in white rabbits. [221]

The antitryptic activity of rabbit serum is said to increase after ultraviolet irradiation.[222]

Giaume [223] claimed that irradiated normal horse serum does not produce anaphylactic shock in sensitized guinea pigs. Five minutes of irradiation of the sensitized animal lessens the shock produced by normal serum. Severe and even fatal shocks result when both the sensitizing agent and the shock-producing material have been irradiated. Brotzu [224] finds daylight or light in the range 5100 to 7700A to be more effective than blue-violet light or darkness in aiding the production of agglutinins in guinea pigs injected with the Gaertner bacillus or with the cholera vibrio. Infrared rays stimulated more agglutinin formation than daylight, and ultraviolet rays more than blue-violet light. Guinea pigs exposed to infrared rays produce more bacteriolysins than those exposed to ultraviolet light.

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[211] Tataranu, F., *Compt. rend. soc. biol.*, **97**, 1736 (1927); *Chem. Abs.*, **22**, 1799 (1928).

[212] Albela, D., *Deut. med. Wochschr.*, **48**, 1347 (1922); *Chem. Abs.*, **17**, 140 (1923).

[213] Koopman, J., *Deut. med. Wochschr.*, **50**, 277 (1924); *Chem. Abs.*, **18**, 2197 (1924).

[214] Gordon, J., and Wormall, A., *Biochem. J.*, **22**, 909 (1928).

[215] Osborn, T. W. B., *Biochem. J.*, **25**, 2136 (1931).

[216] Mesik, R. E., *Arch. sci. biol. (U.S.S.R.)*, **40**, 31 (1936); *Chem. Abs*, **31**, 6726 (1937).

[217] Matushita, M., *J. Chosen Med. Assoc.*, **22**, 787 (1932); *Chem Abs.* **27**, 2208 (1933).

[218] Bessemans, A., and Seldeslacht, A., *Compt. rend soc. biol.*, **99**, 628 (1928); *Chem. Abs.*, **23**, 435 (1929).

[219] Heuer, G., and Potthoff, P., *Centralbl. Parasitenk.*, **I**, **88**, 299 (1922); *Chem. Abs.*, **17**, 144 (1923).

[220] Wenger, W. J., *Z. Immunitats* **93**, 501 (1938); *Chem. Abs.*, **32**, 9248 (1938).

[221] Abe, G., *Sei-i-kai Med. J.*, **56**, No. 11, 2169 (1937); *Chem Abs.*, **32**, 5438 (1938).

[222] Yamanaka, G., Sei-i-kwai; *Med. J.*, **48**, 3, 62 (1929); *Chem. Abs.*, **23**, 4263 (1929).

[223] Giaume, C., *Pediatria Rivista*, **35**, 1111 (1927); *Pathologica*, **20**, 236 (1928); *Chem. Abs.*, **22**, 2202 (1928).

Exposure of guinea pigs to red, yellow or blue light has no effect on the formation of anti-sheep hemolysins.[225]

It has been said that serums obtained from rabbits inoculated with organisms grown on ultraviolet-irradiated agar show greater agglutinating, bacteriolytic and complement materials than those in the production of which the organisms had been grown on ordinary agar.[226]

There have been several recent investigations of the effect of ultraviolet light upon antigens. Intensive irradiation of horse serum for twenty to forty minutes destroys its ability to cause the characteristic anaphylactic contraction of the isolated uterus of guinea pigs sensitized to horse serum. The treated serum retains its ability to desensitize the uterus and after exposure to the treated serum, the uterine horns will no longer react with fresh, untreated serum. This densitization, however, requires a longer period than that produced by untreated actively shocking serum.[227] Different results were reported by Kitamura and Murayama [228] who found 0.1 cc. of thirty minute-irradiated horse serum or egg-white to produce the usual contraction of the uterus of sensitized guinea pigs. After washing and the lapse of twenty minutes, the addition of 0.5 cc. of normal serum also produced a contraction, indicating that desensitization had not been attained. Then, after ten minutes, the addition of neither serum produced contraction.

The agglutinogens of red blood cells, which are said not to contain protein, are not affected by ultraviolet light.[229]

Heuer [230] reported that antibodies are sensitive to ultraviolet rays when diluted. The agglutinins for cholera and paratyphoid A were believed less resistant to ultraviolet rays than those for typhoid, although this was controverted by Ninomiya.[231] Heuer believed the bateriolysins less resistant than the agglutinins. Brawn [282] found ultraviolet light to destroy complement but to have no effect on cholesterolized antigen or on Wassermann negative or positive human serums. Gordon and Wormall [283] found that the destruction of serum complement is not due to oxidation, although the rate of inactivation appeared to be slightly less in a vacuum than in air. It is the heat-labile protein component that is most affected. Levine [284] attributes the destruction to the coagulation of certain protein components.

[224] Brotzu, G., *Boll. soc. ital. biol. sper.*, **8**, 1722 (1933); *Chem. Abs.*, **28**, 4470 (1934).

[225] Diacono, H., *Arch. Inst. Pasteur Tunis*, **20**, 48 (1931); *Chem. Abs.*, **25**, 4312 (1931).

[226] Marras, F. M., and Omar, W., *J. Egyptian Med. Assoc.*, **17**, 687 (1934); *Chem. Abs.*, **28**, 7288 (1934).

[227] Kallós, P., and Kallós-Deffner, L., *Klin. Wochschr.*, **14**, 392 (1935); *Chem. Abs.*, **30**, 3058 (1936).

[228] Kitamura, S., and Murayama, M., *Klin. Wochschr.*, **16**, 88 (1937); *Chem. Abs.*, **31**, 3555 (1937).

[229] Dujarric de la Rivière, R., and Kossovitch, N., *Ann. inst. Pasteur*, **55**, 331 (1935); *Chem. Abs.*, **30**, 4206 (1936).

[230] Hever, G., *Centralbl. Bakt. Parasitenk.*, **I**, **88**, 380 (1922).

[231] Ninomiya, R., *Z. Immunitäts.*, **39**, 494 (1924); *Chem. Abs.*, **18**, 2555 (1924).

[232] Brawn, G., *Z. Immunitats.*, **44**, 27 (1925); *Chem. Abs.*, **20**, 1267 (1926). See also Bovie, W. T., *J. Med. Research*, **38**, 335 (1918).

[233] Gordon, J., and Wormall, A., *Biochem. J.*, **22**, 909 (1928).

[234] Levine, B. S., *Am. Med.*, **35**, 610 (1929); *Chem. Abs.*, **24**, 2174 (1930). See also Friedberger, E., and Scimone, V., *Z. Immunitäts.*, **37**, 341 (1923); *Chem. Abs.*, **18**, 551 (1924).

Hassko[235] states that complement, the antibodies in positive human serums, amboceptors, agglutinins and precipitins all lose their specific activity partly or completely under the influence of ultraviolet rays, the extent depending upon the dilution of the protein, its colloidal properties and various other conditions. Egg albumin irradiated for nine hours is non-precipitable by neoarsphenamine. Paic and Haber[236] find the inhibiting action of mixed light on complement to be appreciable after thirty minutes of irradiation. Destruction is complete after ten hours. Petterson[237] maintains that ultraviolet rays are more active than visible light in inactivating *in vitro* the bactericidal substances of the body. Serum alexin is much more sensitive than β-lysin and the bactericidal substances of white blood cells. Active β-lysin is as sensitive as the inactivated substance. Blanchard[238] finds the opsonic activity of normal cat serum decreased on exposure to a mercury-arc lamp. He suggests that irradiation inactivates the opsonins, which are probably protein-like, by changing their colloidal state.

Growth. Studies have been made of the effect of daily irradiations of animals upon their growth. Leigh-Clare[239] found that, if their eyes were shielded, exposures of young growing rats for periods up to thirty minutes daily had no deleterious effect. Suzuki and Hatano[240] concluded from a series of experiments with white rats, chickens and rabbits, that the ultraviolet rays present in ordinary daylight are far from sufficient for the vigorous development of young chicks.

The rate of growth or the histological anatomy of the thyroid gland of rats is unaffected by daylight, darkness or ultraviolet light environments during their growth, according to Mayerson.[241]

Tadpoles receiving dried milk from thyroidectomized, nonirradiated goats were found by Kucera and Soos[242] to grow slowly and develop abnormally small thyroids. If the udder of the thyroidectomized goat was irradiated, the retarding effect of the milk on the tadpoles was decreased, but they did not develop as fast as those receiving milk from normal goats. The milk from irradiated thyroidectomized goats receiving potassium iodide permitted more rapid development. Rats kept in darkness have an average blood iodine of 25 γ per cent. In the dried thyroid gland there is 211 γ per cent.[243] The gland has the histological picture of increased activity, that is, less colloid, an increased number of follicles and high irregular epithelial cells. Rats given Vigantol or ultraviolet irradiation have a high blood iodine (30 to 40 γ per cent), a low thyroid iodine content (112-167 γ per cent) and the histologic picture of increased colloid and flat, resting epithelium.[244]

Effects on the Secretory Activity of Glands. Doses of ultraviolet light strong enough to cause a rapid erythema exert a histamine-like effect upon gastric secretions, causing the appearance of free hydrochloric acid in patients with so-called histamine achylia, according to Diehl.[245] Sunbaths are also said to stimulate gastric secretion.[246] The usual daily variations in the acidity of the gastric juice are, however, so great as to make definite conclusions somewhat uncertain.[247] Considerable decreases in the secretory activity of the pancreas occur from three to five hours after fifteen to thirty minutes of irradiation of dogs.[248] With shorter irradiation periods (seven minutes) the effects were variable. The effect is attributed to a substance brought to the gland by the blood and produced originally by the irradiation.

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[235] Hassko, S., *Biochem. Z.*, **226**, 462 (1930).

[236] Paic, M., and Haber, P., *Compt. rend.*, **198**, 613 (1934).

[237] Petterson, A., *Z. Immunitats.*, **75**, 156 (1932); *Chem. Abs.*, **26**, 5646 (1932).

[238] Blanchard, E. W., *Physiol. Zoöl.*, **4**, 316 (1931); *Chem. Abs.*, **25**, 4599 (1931).

[239] Leigh-Clare, J. L., *Biochem. J.*, **21**, 208 (1927).

[240] Suzuki, K., and Hatano, T., *Bull. Agr. Chem. Soc. Japan*, **3**, 14; *Chem. Abs.*, **22**, 1182 (1928).

[241] Mayerson, H. S., *Am. J. Physiol.*, **113**, 659 (1935). See, however, Bennholdt-Thomsen and Ziegler-Wellmann.[243]

[242] Kucera, C., and Soos, M., *Compt. rend. soc. biol.*, **113**, 619 (1933); Andrik, L., and Kucera, C., *Ibid.*, 622; *Chem. Abs.*, **27**, 4564 (1933).

[243] Bennholdt-Thomsen, C., and Ziegler-Wellmann, M., *Klin. Wochschr.*, **13**, 800 (1934); *Chem. Abs.*, **28**, 6734 (1934).

[244] For the effect of ultraviolet rays on lymphoid tissue, see Jolly, J., *Compt. rend. soc. biol.*, **93**, 999 (1925).

[245] Diehl, F., *Arch. exptl. Path. Pharmakol.*, **159**, 367 (1931).

Gedda [249] finds a fifteen-minute irradiation of human subjects to have a diuretic effect, increasing not only the volume of urine but also its content of urea and especially of chlorides.

Light treatment particularly by visible rays, increases the accumulation of zinc [250] in the tissues of animals to which the metal is administered over that of animals receiving the same amount but not irradiated. Pincussen has discussed [251] the acceleration of the excretion of lead brought about by irradiation. Pincussen and Roman[252] demonstrated that irradiation by the mercury arc increases the ratio of organic to inorganic iodine in both normal and dye-injected mice. It also increases the organic bromine at the expense of the inorganic bromine but has no similar effect upon the distribution of chlorine.

A number of experiments have been made upon portions of non-intact animals. Azuma and Hill [253] found irradiation of involuntary muscle by ultraviolet rays antagonized the action of adrenalin but not that of emetine. These rays increase the tone and rhythmic contractions of the muscle of the frog rectum if there is calcium in the nutrient fluid employed.[254] In the presence of magnesium, however, they cause relaxation and cessation of rhythmic contractions. The presence of calcium ions is also necessary for ultraviolet rays to stimulate the contraction of skeletal muscle suspended in Tyrode's solution. Potassium and magnesium ions appeared to moderate the effect of the calcium ions.[255]

Petersson [256] believes ultraviolet light weakens the parasympathetic excitability of the surviving intestine and uterus by diminishing the excitability of the sympathetic inhibitor and increasing that of the sympathetic motor. These modifications of excitability are thought to be durable and to persist after the cessation of the irradiation.

Ultraviolet light directly stimulates the contracture of skeletal muscle of the frog independently of the presence of molecular oxygen.[257] The redox potential is increased, the maximum effect being produced by ten minutes of irradiation.[258] Larger doses inhibit the change. The effect is produced immediately after the exposure to ultraviolet rays. For the effect to occur, the dehydrogenase and hydrogen donor system must be present. At an optimum dosage, the reduced glutathione increases, the reverse occurring when excessive doses are used. Ashkenaz finds stimulation by ultraviolet light causes muscle fibers to give off calcium.[259]

It has been shown by Kler [260] that under suitable conditions, ultraviolet rays stimulate a rhythmic contraction of the heart *in vitro*. The cardiac effects of atropine are also influenced by irradiation of a human subject to whom it is administered, according to

[246] Barone, V. G., *Arch. Fisiol*, **31,** 468 (1932); *Chem Abs*, **27,** 1667 (1933).

[247] Keller, P., and Loeb, M., *Klin Wochschr*, **4,** 2390 (1925); *Chem. Abs.*, **20,** 922 (1926).

[248] Glikson, E. B., *Arch. sci biol. (U.S.S.R.)*, **39,** 629 (1935); *Chem. Abs*, **30,** 6023 (1936).

[249] Gedda, L., *Minerva Med.*, **I,** 841 (1933); *Chem Abs.*, **27,** 4300 (1933).

[250] Nakadate, K., *Biochem Z.*, **265,** 61 (1933).

[251] Pincussen, L., *Klin. Wochschr*, **12,** 275 (1933).

[252] Pincussen, L., and Roman, W., *Biochem. Z.*, **216,** 3336 (1929)

[253] Azuma, Y., and Hill, L., *Proc. Roy. Soc.*, **99B,** 221 (1926).

[254] Azuma, Y., *Proc. Roy. Soc.*, **100B,** 431 (1926).

[255] Azuma, Y., *Proc. Roy. Soc.*, **101B,** 24 (1927).

[256] Petersson, F., *Compt. rend. soc. biol.*, **99,** 1677 (1928); *Chem. Abs*, **23,** 622 (1929).

[257] Spealman, C. R., and Blum, H. F., *J. Cellular Comp Physiol.*, **3,** 397 (1933).

[258] Uchimura, T., *J. Biochem. (Japan)*, **25,** 207 (1937); *Chem. Abs.*, **31,** 5395 (1937).

[259] Ashkenaz, E. W., *J. Cellular Comp. Physiol.*, **12,** 139 (1938); *Chem. Abs.*, **32,** 9112 (1938).

[260] Kler, S., *Compt. rend. soc. biol.*, **93,** 1391 (1925); *Chem. Abs.*, **20,** 1821 (1926); see also Wastl, H., *Arch. exptl. Path. Pharmakol.*, **114,** 56 (1926).

Garot.[261] When administered immediately after the irradiation of children it causes an acceleration of the pulse rate more rapidly but less marked than in the case of non-irradiated subjects.

A substance present in alcoholic extracts of skeletal muscle which stimulates the action of the isolated toad heart is not affected by irradiation, according to Oana.[262] Haberlandt[263] believes the stimulating substance which may be extracted from the heart of the frog in Ringer's solution can be partly, but not completely, destroyed by ultraviolet light. In this respect he thought it to resemble adrenaline and the accelerating substance of Loewi.

Offant and Dubouloz[264] claimed that the rhythm of the perfused frog heart can be affected by the use of irradiated Ringer's solution as the perfusion fluid, unless the solution had been kept at 100° during irradiation. Renosto,[265] however, found that, in the absence of sensitizers, ultraviolet irradiation of either the heart itself or the perfusion fluid had no effect. In the presence of dyestuffs in the perfusion liquid there could be observed, after a latent period following irradiation, a lessened amplitude of the contractions of the heart without any change in the tone, rhythm or frequency.

Recently, Guttman[266] found that after the rhythm of frog or Limulus hearts had been stopped by the addition of an excess of potassium to the perfusion fluid, it could be promptly restored by ultraviolet irradiation. He also noted[267] that irradiation of the clam heart in sea water for two or three minutes caused a marked increase in tonus and a definite decrease in amplitude, but that the pace-maker was not affected. It was suggested that irradiation may increase the permeability of the cells, permitting potassium to leave and calcium to enter. The rate of the Limulus heart in sea water was increased by ultraviolet irradiation. The same effect was observed when the heart was shielded from the rays and masses of skeletal or smooth muscle were irradiated instead. This was explained by the assumption of the production of an accelerator substance in these tissues which diffuses to the heart About twenty minutes after the cessation of the irradiation, the frequency and amplitude are diminished, possibly because of the formation of a depressor substance.[268]

Milk. In women, ultraviolet irradiation appeared to increase the quantity of milk secreted in ten of fifteen cases studied by Lesné and Dreyfus-Sée.[269] Aside from an increase in the antirachitic properties of the milk, its chemical composition was unaffected. Knott and Garver[270] found that irradiation of the udders of cows for twenty minutes daily for 21 days had no significant effect upon the quantity of milk produced or on the content of its butter fat or total solids.

Martini[271] finds the milk of various species of animals to exhibit different powers of reducing methylene blue in light. The most active is that of sheep. Cows' milk loses this power very easily, especially if exposed to light. The property is ascribed, not to the fatty components of the milk, but rather to a thermostable, water-soluble substance, possibly glutathione.

The oxidation-reduction potentials of cream and whole or skimmed milk drift toward the negative side on exposure to light.[272] This potential change is accentuated by the addition of methylene blue. As the solutions develop a progressively more negative potential, methylene blue becomes decolorized when this potential reaches that capable of reducing the dye. Similarly, the blue color reappears when the solution develops a potential sufficiently positive to oxidize the dye. The addition of fat to skimmed milk hastens the reduction time of methylene blue in samples exposed to sunlight, probably because of the tendency of the fat to elevate the zone of reduction. However, the reducing intensity induced by the growth of bacteria is more negative than that induced by sunlight. This indicates that the photoreduction of methylene blue in milk is a reaction distinct from that produced by bacteria. When skimmed milk containing methylene blue decolorized by sunlight is placed in darkness, the potential quickly becomes sufficiently positive to oxidize the leuco-base. Artificial light hastens the reduction of methylene blue in market milk. Light from a 75-watt electric bulb produces a potential drift in milk which differs only in degree from that observed in sunlight. Similar observations that the oxidation of fat in whole milk under the influence of sunlight causes the development of a reducing potential detected by its effect upon methylene blue or electrometrically were made by Whitehead.[273]

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[261] Garot, L., *Compt. rend. soc. biol*, **96**, 1048 (1927); *Chem Abs.*, **21**, 2333 (1927).

[262] Oana, M., *Japan. J. Exptl. Med.*, **10**, 123 (1932); *Chem. Abs.*, **26**, 4852 (1932).

[263] Haberlandt, L., *Arch. ges. Physiol., (Pflüger's)*, **218**, 129 (1927); *Klin. Wockschr*, **6**, 2099 (1927).

[264] Offant, C., and Dubouloz, P., *Compt. rend. soc. biol.*, **112**, 373 (1933); **115**, 1300 (1934); *Chem. Abs.*, **28**, 4479 (1934).

[265] Renosto, G., *Boll soc. ital. biol. sper.*, **10**, 295 (1935); *Chem Abs.*, **29**, 6308 (1935).

[266] Guttman, S. A., *J. Cellular Comparative Physiol.*, **8**, 37 (1936); *Chem. Abs.*, **30**, 5662 (1936).

[267] Guttman, S. A., *Proc. Soc. Exptl. Biol Med*, **33**, 363 (1935); *Chem. Abs.*, **30**, 8250 (1936).

[268] Guttman, S. A., *Biol Bull.*, **72**, 75 (1937).

[269] Lesné, E., and Drefus-Sée, G., *Lait*, **11**, 155 (1931); *Chem. Abs.*, **25**, 4032 (1931).

[270] Knott, J. C., and Garver, H. L., *Ann. Report Washington Agr. Expt Sta., Bull.* **260**, 27 (1931); *Chem. Abs.*, **26**, 4615 (1932).

[271] Martini, V., *Boll. soc. ital. biol. sper.*, **6**, 773 (1931); *Chem. Abs.*, **26**, 1631 (1932).

[272] Aikins, G. A., and Fay, A. C., *J. Agr. Research*, **44**, 85 (1932); *Chem. Abs.*, **26**, 3045 (1932); Martini, E., *Biochem. Z.*, **260**, 153 (1933).

EFFECTS OF ULTRAVIOLET LIGHT UPON THE EYE MEDIA

As the sense-organ of reception of solar radiations, the retina would seem to require especial protection. It is, therefore, not surprising that the structures of the eye through which the rays must pass in order to reach the retina act as filters of potentially injurious rays. Against natural ultraviolet the cornea affords little protection, as it is transparent to rays of wave-length greater than 2950A.[274] The vitreous and aqueous humors transmit the ultraviolet down to 3000A, according to Birch-Hirschfeld.[275] It is the lens of the eye which is chiefly responsible for stopping ultraviolet rays from reaching the retina.

de Chardonnet [276] used a quartz plate coated with a silver film of such a thickness as to be opaque to the visible and invisible spectrum except for the region between 3010 and 3430A. Through this plate normal eyes could not see an arc light, but eyes from which the lens had been removed in the operation for cataract could detect the movements of the arc.

In addition to its absorptive power, the lens can alter the rays by fluorescence. The fluorescence is excited by rays between 3500 and 4000A. Thus we see that no radiation of wave-length shorter than 3500 (or more probably 3800A) can reach the retina. In the later period of life, owing to yellowing of the media, the limit is pushed into the most refrangible region of the visible spectrum. Opinions differ greatly as to the limit of visibility. Some claim to have seen the line in the tin spectrum at 3175A.[277] This may possibly have been due to stray reflections in the monochromators employed. Saidman and Dufestel [278] claim to have seen faintly a line at 3650A.[279]

Exposure of the eyes to ultraviolet rays results in inflammation, but only of the superficial structures. This effect, which has been described in Chapter 10, is strictly comparable with the inflammations of the skin which are intentionally provoked as part of the routine of ultraviolet therapy. Like these, the conjunctival inflammation subsides rapidly without leaving any trace. It is rarely desirable to produce such a reaction. Verhoeff and Bell,[280] who made elaborate studies of the reaction, conclude that conjunctivitis is caused by rays of wave-lengths shorter than 3050A.

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[273] Whitehead, H. R., *Biochem. J.*, **25**, 1647 (1931).

[274] Martin, E. K., *Proc. Roy. Soc.*, **85**, 319 (1912); Schanz, F., and Stockhausen, K., *Arch. für Ophth.*, **69**, 49 (1908).

[275] Birch-Hirschfeld, A., *Arch. für Ophth.*, **71**, 573 (1909).

[276] de Chardonnet, *Compt. rend.*, **96**, 509 (1883).

[277] Glancy, A. E., *Am. J. Physiol. Optics*, **4**, 145 (1923); Graham, W. P., *J. Opt. Soc. Am.*, **6**, 605 (1922).

[278] Saidman, J., and Dufestel, L. G., *Compt. rend.*, **182**, 1173 (1926).

[279] For a very detailed study of the transmission of the various media of the eye and of the eye as a whole, see Shoji, Y., *Mitt. Med. Fak. Univ. Tokoyo*, **29**, 61 (1922). This is discussed in Laurens, H., "The Physiological Effects of Radiant Energy," p. 150. New York, The Chemical Catalog Co., Inc., (Reinhold Publishing Corp.), 1933.

Many studies have been made upon the lens, particularly because of the possibility of a relation to the ultraviolet rays of sunlight and the production of cataracts. Burge [281] concluded that ultraviolet rays can change cell protoplasm in such a manner that certain salts may combine with it to form a precipitate or coagulum. Abnormal amounts of sodium silicate or calcium salts in the cells of the eyelids or the cornea augment the inflammatory action of the radiations. By exposing fish, living in dilute solutions of certain salts, to ultraviolet rays, he was able to produce cataracts.

The observations of Schanz [282] on the lens have shown that the effect of light is to render its proteins less soluble. The frequency of lenticular opacity in diabetes suggested a series of experiments in which equal amounts of a protein solution in each of a series of quartz test tubes were irradiated in the presence of increasing amounts of acetone. The results showed that the loss of solubility of the protein is increased by the presence of acetone.

Adams [283] finds that, although in patients with senile cataracts the serum calcium is appreciably higher than normal, calcium salts acting on fresh ox lenses do not cause opacity unless present in non-physiological concentrations. Nor could she find them to act as sensitizers to ultraviolet radiations as had been suggested by Burge.

All wave-lengths, including infrared, visible and ultraviolet, are said by Burge, Wickwire and Schamp [284] to be capable of rendering the lens material electronegative and so being effective in producing its calcification. It is difficult to explain this behavior of the longer wave-lengths physically and these authors note the shorter wave-lengths to be much the more effective. Hinrichs [285] suggests that the effect of ultraviolet irradiation of excised lenses in 0.1- to 1-per cent solutions of sodium chloride and calcium chloride is probably a surface phenomenon. There is involved a change in the permeability to salts or their ions and a subsequent precipitation of the lens protein. Calcium is more effective than sodium in producing the lens opacity.

Opinion at present does not ascribe the origin of cataracts in glass workers to visible rays and probably not to the direct action of either the infrared rays or the ultraviolet rays. Bradford and others suggested [286] the possibility that an indirect action on the nutrition of the lens may be ascribed to the action of the infrared rays on the iris and ciliary bodies.[287]

Lieben and Kronfeld [288] illuminated the lenses of fresh intact pigs' eyes with diffused daylight in the presence of a sensitizer and also by a quartz lamp both with and without a sensitizer. In no case could there be observed any decrease in the tryptophane content of the lens proteins. Under the same conditions in solutions of the lenses in alkali, containing the equivalent of 0.5 per cent of protein, considerable destruction of this amino- acid occurred, but since the destruction did not occur in solutions four times as concentrated, it was assumed that the protein of the lens is protected in high concentrations from chemical changes due to light. Normal human lenses and those with cataracts showed no difference in the tryptophane content of their protein.

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[280] Verhoeff, F. H., and Bell, L., *Proc. Am. Acad. Arts Sci.*, **51**, 640 (1916).

[281] Burge, W. E., *Am. J. Physiol.*, **39**, 335 (1916).

[282] Schanz, F., *Arch. ges. Physiol. (Pflüger's)*, **170**, 646 (1918); *J. Chem. Soc.*, **118**, II, 213 (1920).

[283] Adams, D. R., *Biochem. J.*, **23**, 902 (1928).

[284] Burge, W. E., Wickwire, G. C., and Schamp, H. M., *Arch. Ophthalmol.*, **17**, 234 (1937); *Chem. Abs.*, **31**, 3133 (1937).

[285] Hinrichs, M., *Proc. Soc. Exptl. Biol. Med.*, **27**, 535 (1930).

[286] Report of Glass Workers' Cataract Committee, *Proc. Roy. Soc.*, **103B**, 192 (1928).

[287] Note also Sheard, C., *Am. J. Physiol. Optics*, **5**, 214 (1924).

[288] Lieben, F., and Kronfeld, P., *Biochem. Z.*, **197**, 136 (1928).

The ability of the lens to oxidize certain organic acids (fumaric, malic and succinic) is decreased by exposure to ultraviolet light.[289]

The glutathione content of the ox lens is decreased by exposure to ultraviolet light and to a more marked extent by heat rays. Frog eyes not exposed to light show an oxygen consumption of the order of 6.5 cu. mm. per gm. of tissue per minute. This is decreased by exposure to light.[290]

The lactic acid content of the aqueous humor is unaffected by keeping animals in light or darkness.[291] The natural vitreous humor of pH 8.2 absorbs near 2600 to 2700A, differing from the crystalline humor which absorbs at 2760A.[292]

Effects of Ultraviolet Light on Development of Simple Organisms

Lillie and Baskerville[293] in reporting experiments on starfish eggs, state the effects produced in unfertilized eggs by brief irradiation with ultraviolet rays to resemble those of partial activation. The immediate change produced in the egg system is of the same essential nature as that caused by temporary exposure to high temperature or other activating agent. The primary effect of the rays is probably a structural change, that is a change in the colloidal substratum of the protoplasm and probably of the surface layer, upon which follow specific chemical effects as a secondary consequence.

Exposure of the eggs of *Chaetopterus* for sixty to seventy seconds at 21.5 cm. from a mercury arc leads to a tendency of the eggs to fuse, after insemination, during the cleavage stages into masses of twelve to fifteen eggs, because of changes in the cortex.[294]

Irradiation of normal *Arbacia* eggs produces at first a slight increase, then a decrease and finally a complete loss of the power of producing fertilizin.[295] The irradiation of normal egg water produces a fading of the echinochrome pigment, a slight increase in the pH, and a reduction of the agglutination of fertilizin. The more concentrated suspensions of sperm show an increase of viscosity and a decrease of surface tension following irradiation. Irradiated sperms show a reduction of agglutinability by normal egg water. The more dilute suspensions are the more susceptible.

Vlès and Gex[296] found the principal absorption band of sea urchin eggs to be at about 2800A.

The growth of cultures of connective tissue may be inhibited by an eight to ten minutes' exposure to ultraviolet rays, but the cells regain their proliferative power when transferred to a fresh medium. The lethal dose is ten to fifteen times as large.[297]

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[289] Adams, D., *Proc. Roy. Soc.*, **98B**, 244 (1925); *Biochem. J.*, **23**, 902 (1929).

[290] Noyons, A., and Wiersma, C., *Acta Brevia Neerland. Physiol. Pharmacol. Microbiol.*, **3**, 156 (1933); *Chem. Abs.*, **28**, 7337 (1934).

[291] Wittgenstein, A., and Gaedertz, A., *Biochem. Z.*, **176**, 1 (1926).

[292] Abe, T., *Arch. phys. biol.*, **6**, 1 (1927); *Chem. Abs.*, **23**, 3499 (1929).

[293] Lillie, R. S., and Baskerville, M. L., *Am. J. Physiol.*, **61**, 57 (1922); *Chem. Abs.*, **16**, 2937 (1922); *cf.* Baldwin, W. M., *Biol. Bull.*, **37**, 294 (1919); *Chem. Abs.*, **14**, 1164 (1920).

[294] Just, E. E., *Science*, **71**, 72 (1930).

[295] Hinrichs, M. A., *Biol. Bull. Marine Biol. Lab.*, **53**, 416 (1927); *Chem. Abs.*, **22**, 463 (1928).

[296] Vlès, F., and Gex, M., *Bull. Inst. Oceanograph*, **658**, 23 pp. (1934); *Chem. Abs.*, **29**, 2184 (1935).

Chick embryos show a differential susceptibility to ultraviolet irradiation, the regions of greatest physiological activity being the most easily modified by sublethal doses.[298] These same regions also die and disintegrate the most rapidly on the application of lethal doses. In the embryonic stages there is a single anteroposterior gradient of susceptibility which in later stages is complicated by the appearance of local regions of high susceptibility. In general, the susceptibility to the modification of development by ultraviolet irradiation is proportional to the dosage.

The effects of local ultraviolet irradiation of developing embryos of *Triton taeniatus* are largely limited to the surface cells, according to Dürken,[299] probably on account of the great light absorption by the yolk granules. The result is a pigmentation of the irradiated area, followed by a contraction of the surface of the cell, which forces out its contents. In the later stages of development, irradiation kills the entire cell on which it falls, and the dead cell is either thrown out or, in still older embryos, remains within the organism without undergoing further development. Irradiation of the organizer region of the *Triton* embryo can completely or partially inhibit the organizing action without killing the embryo.[300] Since the active substance appears to be very stable, its direct inactivation by light seems improbable. Reith, however, regards the power of induction by the organizer region (blastopore lip) when implanted in normal gastrulae as very resistant to ultraviolet radiations.[301]

To determine the nature of the colloidal changes which occur in irradiated protoplasm, Remotti[302] bred some of the young of *Salmo lacustris* in darkness and exposed others to a 1000 c.p. electric light. The serum drawn from the irradiated and sectioned embryos reacted more slowly with hydroquinol than that from non-irradiated ones.

Chick embryo cells grown in media containing cancer-producing hydrocarbons are photosensitive. Methylcholanthrene, 1,2,5,6-dibenzanthrene and 1,2-benzopyrene in concentrations of 0.05 to 0.1 per cent do not affect the growth or mitosis of the cells until the cultures are exposed to a bright light. Exposures of two to ten minutes cause changes in the cells and inhibit mitosis, but the cells subsequently recover and proliferate, unless the exposures have been unduly prolonged.[303]

Ultraviolet irradiation of the larvae of *Drosophila melanogaster* does not prolong the larval stage as do x-rays. The immediate effects on carbon dioxide formation were, however, similar, according to Thompson.[304] Small doses of ultraviolet light hasten the development of mosquito larvae, but larger amounts, and also complete darkness, are harmful.[305]

The penetration of acetic acid into the living larvae of frogs occurs more slowly in darkness than in light.[806] If the larvae are exposed to ordinary light, the illumination is followed by no after-effects, but if the quartz lamp is used, a definite influence on the permeability of the larvae remains. The irradiation of tadpoles causes accelerated development, but that of frog and toad spawn is without effect.[807]

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[297] Kler, S., *Compt. rend soc. biol.*, **93**, 1389 (1925); *Chem. Abs.*, **20**, 1821 (1926).

[298] Hinrichs, M. A., *J. Exptl. Zoöl.*, **47**, 309 (1927); *Chem. Abs.*, **22**, 994 (1928).

[299] Dürken, B., *Z. wiss. Zoöl.*, **144**, 123 (1933); *Chem. Abs.*, **28**, 534 (1934).

[300] Dürken, B., *Z. wiss. Zoöl.*, **147**, 295 (1935).

[301] Reith, F., *Z. wiss. Zoöl.*, **150**, 179 (1937); *Chem. Abs.*, **32**, 3490 (1938).

[302] Remotti, E., *Atti accad. Lincei*, **3**, 772 (1926); *Chem. Abs.*, **20**, 3196 (1926).

[303] Lewis, M. R., *Am. J. Cancer*, **25**, 305 (1935).

[304] Thompson, W. R., *J. Gen. Physiol.*, **18**, 869 (1935).

[305] Frost, F. M., Herms, W. B., and Hoskins, W., *J. Exptl. Zoöl.*, **73**, 461 (1936); *Chem. Abs.*, **30**, 8404 (1936).

Higgins and Sheard[808] stated in respect to the early larval development of *Rana pipiens* that the stimulative action of light is due to the region between 4000 and 2800A and that lethal effects are due to wave-lengths shorter than 2800A. Ultraviolet rays stimulate the exogenous growth of cells and of the organism as a whole. However, they inhibit subsequent exogenous metabolic processes and therefore interfere with growth and cause death.

Neoplasms. The excess of nuclein phosphorus in cancerous tissue over that in normal tissue observed by Enselme and Enselme[809] disappears after ultraviolet irradiation. On the other hand, lipid phosphorus increases in the irradiated tumor at the same time as the proportion of fat. Under the influence of irradiation, the tendency is for the nuclear constituents to be decreased and for the cancerous tissue to be transformed into fat.

Strong irradiation with ordinary incandescent lamps seemed to accelerate the development of papillomas and cancers in mice treated with tar by Vlès, de Coulon and Ugo.[810]

Lecithin, especially after irradiation with ultraviolet light for 24 to 600 hours is said by Roffo[811] to inhibit the growth of sarcoma cells *in vitro*.

Roffo and Pilar[812] called attention to a possible relation between the increased cholesterol content of skin irradiated by ultraviolet light and the formation of tumors. They observed that 92 per cent of the skin tumors of the face occurred on the parts directly exposed to the sun. Keratotic carcinomas follow hyperkeratotic injuries to the skin exposed to the sun.[813]

They occur particularly in blondes; pigmented skins are more resistant to the light. All of the cases studied gave a history of long exposure to the sun and only 3.62 per cent were less than forty years of age. Roffo[814] exposed ten rats to ultraviolet light. Three died within a few days. The remaining rats were exposed to gradually increasing doses for two weeks and then to a continuation of the last dose for seven or eight months. All these animals developed tumors, multiple keratoses, papillomas, carcinomas and sarcomas. The common sites of the tumors were the regions naturally free from hair, such as the ear, the conjunctiva, or regions from which the hair had been removed. In one animal there was a spindle cell sarcoma on one ear and a carcinoma on the other.

On the other hand, Seel and Carls,[815] find ultraviolet irradiation to inhibit the formation of metastases in rabbits injected with the Brown-Pierce sarcoma. It was even able to prolong their lives.

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[806] Van Herwerden, M. A., *Protoplasma,* **8,** 413 (1929); *Chem. Abs.,* **25,** 3405 (1931).

[807] Abderhalden, E., and Hartmann, J., *Arch. ges. Physiol. (Pflüger's),* **218,** 261 (1927); *Chem. Abs.,* **22,** 1810 (1928).

[808] Higgins, G. M., and Sheard, C., *J. Fxptl. Zoöl.,* **46,** 333 (1926); *Chem. Abs.,* **21,** 3236 (1927).

[809] Enselme, J., and Enselme, J., *Compt. rend ,* **184,** 1353 (1927).

[810] Vles, F., de Coulon, A., and Ugo, A., *Arch phys. biol ,* **12,** 255 (1935); *Chem. Abs.,* **30,** 1862 (1936).

[811] Roffo, A. H., *Bol. inst. med. exptl. estudio cancer, No. 41,* 4 (1936); *Chem. Abs.,* **31,** 4393 (1937).

[812] Roffo, A. H., and Pilar, F., *J. Physiol. Path Gen.,* **28,** 854 (1934); *Chem. Abs.,* **25,** 2478 (1931)

[813] Roffo, A. H , *Neoplasmes,* **12,** 257, 521 (1933).

[814] Roffo, A. H , *Ibid.,* **13,** 129 (1934); *Chem. Abs.,* **29,** 507 (1935).

[815] Seel, H., and Carls, H., *Z. Krebsforschung,* **40,** 416 (1934); *Chem. Abs.,* **28,** 3787 (1934).

Miscellaneous Effects on Various Organisms

Henri and Mme. Henri[316] have shown that ultraviolet rays produce involuntary movements in small animals, that a fixed minimum exposure (initial period) is required to produce this effect, and that a definite time (latent period) elapses between the termination of the initial period and the movement. The results show that during the initial period photochemical reactions take place in the peripheral organs and that the products of these reactions are distributed by diffusion and osmosis. The initial and latent periods are not affected by change of temperature. Prolonged exposure to ultraviolet rays renders *Cyclops* immobile, but it responds to ultraviolet rays and the "initial period" is then longer, but gradually returns to its primitive value. This is also the case with an animal in which the nerve terminals have been etherized. The phenomenon of fatigue and the recovery of excitability by ultraviolet radiation, therefore, has its seat in the peripheral organs.

Hinrichs[317] maintains that the amount of irradiation in a given spectral region absorbed by the protoplasm in a given period of time determines whether there is to be an increase or a decrease in the rate of the physiological processes.

The respiration of *Calanus finmarchius* may be increased 100 per cent by light, according to Marshall, Nicholls and Orr.[318]

The photolytic action of light on the luminescent granules of the ctenophore, *Euchoris multicornis,* according to Moore,[319] conforms to the Bunsen-Roscoe law; it proceeds as a first-order reaction and is not accelerated by a rise in temperature.

Recent observations by Kuhn, Moewus and Jerchel[320] indicate that illumination of an aqueous suspension of the gametes of *Chlamydomonas eugamentos* leads to the formation of certain substances which pass into the surrounding solution, and enable it, when added to a dark culture of gametes, to cause them to develop motile flagella and to fuse. These substances may also be destroyed by prolonged exposure of the solutions to light. The motility and development of flagella is produced by red, yellow, green, blue and total visible light, but fusion is produced only by blue and ultraviolet light. These authors have concentrated the motility substance obtained by illumination of gametes with a 500-watt lamp, obtaining it as an orange-yellow dye, which after hydrolysis yielded in chloroform a spectrum similar to that of *trans*-crocetin. The original substance may be a glucoside of crocetin, similar to the crosin of saffron. The fusion substances, different for the male and female gametes, have not yet been concentrated. The precursor is exceedingly sensitive to light. The light-transformed product is an orange-yellow, chloroform-soluble dye with properties similar to those of *trans*-crocetin dimethyl ester. The *cis* form of crocetin dimethyl ester easily rearranges to the *trans* form in blue or violet light.

The absorption spectrum of the porphyrin obtained by extracting the integument of earthworms in darkness is rather rapidly altered by irradiation with light.[321]

Mitogenetic Radiations. In 1923, Gurwitsch[322] claimed that certain biological systems, such as the root tips of onion at certain periods of development, emit radiations in the short ultraviolet which may be detected by their ability to stimulate the growth of other tissues. These rays are called mitogenetic radiations. An extremely large number of papers deal with this phenomenon, but as yet its existence can scarcely be said to be established. The radiations are usually stated to lie within the wave-length range of 1900 to 2500A, but to be emitted in such low intensities (about 100 quanta per sq. cm. per second) that only by the use of a Geiger counter could they be physically detected. Some competent observers using this method have failed to detect any evidence of their existence.[823] Most who claim their existence have used biological systems for their detection. In view of the uncertainty which surrounds this field no further discussion will be given here of the more than six hundred recent papers concerning this alleged phenomenon. The reader is referred to the critical reviews of Hollaender and Claus.[824, 825] It is said that the origin is one of several chemiluminescent reactions such as oxidation, glucolysis, hydrolysis, splitting of nucleic acid, etc. It has even been stated that such processes as the setting of plaster of Paris emit ultraviolet rays detectable only by their ability to produce a pigmentation of the skin. Closely related are the necrobiotic rays which Lepeschkin believes to be emitted during the decomposition of constituents of cells which have just died.[826]

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[316] Henri, V., and Henri, Mme., *Compt. rend.,* **155,** 414 (1912); *J. Chem Soc.,* **102,** 964 (1912).

[317] Hinrichs, M., *Proc. Soc. Exptl. Med. Biol.,* **26,** 175 (1928).

[318] Marshall, S. M., Nicholls, A. G., and Orr, A. P., *J. Marine Biol. Assoc.,* **20,** 1 (1935); *Chem Abs.,* **29,** 3045 (1935).

[319] Moore, A. R., *J. Gen. Physiol.,* **8,** 303 (1926).

[320] Kuhn, R., Moewus, F., and Jerchel, D., *Ber.,* **71B,** 1541 (1938).

[321] Kobayashi, S., *Sci., Repts. Tohôku Imp. Univ.,* **5,** 763 (1930); *Chem. Abs.,* **25,** 2489 (1931)

[322] Gurwitsch, L., *Arch. Mikrosk. Anat. u. Entw. Mech.,* **100,** 11 (1923).

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[823] Lorenz, E., *U. S. Public Health Repts.*, **48**, 1311 (1933).

[824] Hollaender, A., and Claus, W. D., *J. Opt. Soc. Am.*, **25**, 270 (1935).

[825] Note also the article by Hollaender, A., in Duggar, B. M., "Biological Effects of Radiation," Vol. 2, New York, McGraw-Hill Book Company, Inc., 1936.

[826] Lepeschkin, W. W., *Ber. deut. Bot. Ges.*, **50**, 367 (1932); *Chem. Abs.*, **27**, 316 (1933).

Chapter 37

Therapeutic Applications of Ultraviolet Light Exclusive of Rickets

The health-promoting properties of sunlight have been recognized from the earliest times. The Egyptians treated their sick by exposing them to the sun and the Greeks and Romans had solaria. In the development of medicine, however, actinotherapy received relatively little attention until Finsen in 1893 began a systematic study of the therapeutic uses of light.

Local Therapy. His most notable results were attained in the treatment of lupus (skin tuberculosis) by the rays from a strong carbon arc. Since the source used by Finsen was relatively poor in the effective ultraviolet radiations it was necessary to make prolonged exposures with local pressure for an hour every five days over a period of about six months. The advent of the therapeutic quartz lamp with the improvements described by Kromayer (see Chapter 7) made it possible to shorten the irradiations to but a few minutes. Although Finsen attributed the results to a direct bactericidal action of the rays, it seems, however, that in many cases the bacilli may be lodged too deep for the rays to penetrate to them. Rost, Jessionek and Reyn have suggested that the effect may be indirect since it was found that areas of lupus beyond the immediately irradiated areas also showed improvement.

Dermatologists use this form of treatment for a number of skin diseases other than lupus.[1] The Council of Physical Therapy of the American Medical Association stated that ultraviolet irradiation may produce a favorable effect in the following dermatoses: scrofuloderma, erythema induratum, eczema, psoriasis, parapsoriasis, pustular folliculitis, indolent ulcers, furunculosis, acne vulgaris, angioma serpiginosum, pityriasis rosea. It also is stated that this treatment may induce an attack, cause an exacerbation or produce other injurious effects in the following conditions: eczema, psoriasis, lupus erythematosus, herpes simplex, xeroderma pigmentosum, farmers' skin, and prematurely senile skin. It was held that in some cases the effect of the treatment may be due to a local lethal action upon the superficial diseased cells, which subsequently gradually slough off. In other cases, the effects are due to causes far more complex and as yet but little understood.[2]

Dentists have stated that unfiltered rays from a Kromayer lamp may be employed to advantage in the treatment of sockets after extraction to relieve pain and to promote the formation of new tissue. The usual technique is to precede a one-half to five-minute application of the rays by a thirty-minute application of infrared rays.

Sunlight therapy for local diseased areas was introduced by Bernhard in Switzerland. He states[3] that he first observed the beneficial effects of sunlight upon large intractable wounds in 1902. Bernhard attributed the beneficial effects of sunlight to the entire spectrum rather than to just the ultraviolet region. He considered the more penetrating visible and near infrared radiations to stimulate epithelization. The hyperthermia produced by the infrared rays lessens the pain and increases the local circulation. The direct application of the rays of the quartz mercury-arc lamp to wounds not only fails to provide these beneficial radiations but may be deleterious.

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[1] Russell, W. K., *Am. Med.*, 34, 390 (1928).

[2] American Medical Association, "Handbook of Physical Therapy," 2nd Ed., 1937.

[3] Bernhard, O., cited by Laurens, H., "The Physiological Effects of Radiant Energy," p. 136, New York, The Chemical Catalog Co. (Reinhold Publishing Corp.), 1933.

Rasero[4] however, claimed that good results followed the irradiation of torpid wounds with the mercury arc, and Coulter and Smith found doses of ultraviolet light which produce a mild erythema on normal skin to aid in the treatment of burns and wounds.[5] They also recommend ultraviolet light in the preparation of infected granulation tissue for skin grafting.

Since the water-cooled Kromayer arc emits a large proportion of its energy as wave-lengths shorter than 3000A, it tends to produce more lethal effects than the air-cooled mercury-arc. The radiations from the water-cooled arc described in Chapter 7 may be applied to areas within the body orifices by means of quartz applicators employing the principle of internal reflections. A wide variety of these, vaginal, prostatic, proctoscopic, nasal, sinus and the like, are available.

General Body Therapy. A more recent development is the general irradiation of large surfaces of the body. Among the most brilliant clinical developments of the past few decades have been those reported by Rollier and others on the use of sunlight in the treatment of tuberculosis of the bones and joints. Since these results were obtained in a clinic opened in 1903 at Leysin in the Alps, at an altitude of 1500 meters, they were attributed to the ultraviolet energy abundant in the solar radiations at those altitudes. As yet, however, there can scarcely be said to be general agreement among those who use the methods of heliotherapy most successfully as to which rays of the sunlight are of the greatest value. The problem is obviously complicated, since factors other than sunlight, such as the effects of altitude, fresh air, rest, adequate diet and other therapeutic measures affect the results attained. Thus it is difficult even to evaluate the part in the cure played by sunlight. There is obviously still a need for much experimental work before it will be known which wave-length regions contribute most to the value of this form of therapy.

That heliotherapy can be successfully employed at sea level has subsequently been demonstrated, notably by Sir Henry Gauvain in England. Gauvain attributed much of the value of heliotherapy at sea level to the frequent variations in intensity which are encountered there. It may be recalled that it had been demonstrated by Laurens and Mayerson that fluctuations in light intensity stimulate various physiological processes. Other successful clinics for heliotherapy at low altitudes have been those of Kisch near Berlin, of Phelps in New Haven at Yale,[6] of LoGrasso at Perrysburg, New York,[7] and one at Chestnut Hills in Pennsylvania, described by Eliason.[8]

At some of these clinics, heliotherapy has been supplemented by the use of artificial light sources, particularly during dark seasons and during the months when the ultraviolet radiations in sunlight are reduced in amount. Reyn supplemented the local treatment of lupus at the Finsen Institute with general body irradiations with the carbon arc. Others employ the air-cooled quartz mercury arc for this purpose. Mayer has, for example, stated that peritoneal tuberculosis usually responds to the latter form of treatment. The lethal rays emitted by the mercury arc are reduced considerably in intensity as compared with those of the closely applied water-cooled arc, by the greater distance between the arc and the patient. The present tendency, however, seems toward the use of the carbon arc in solaria for the irradiation of large numbers of patients at one time, since its emission corresponds so much more closely to that of sunlight than does that of the mercury arc. A recent hospital installation is shown in Figure 24 (p. 63).

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[4] Rasero, R., *Riforma Medica Naples*, 38, 772 (1922).

[5] Coulter, J. S., and Smith, E. M., Jr., *Radiology*, 16, 737 (1931).

[6] Phelps, W. M., *J. Bone Joint Surgery*, 12, 253 (1930).

[7] Mayer, E., "Clinical Application of Sunlight and Artificial Radiation," Baltimore, Williams and Wilkins Company, 1926.

[8] Eliason, R. T., *Annals of Surgery*, 88, 947 (1928); note also Armand-Delille, P., *J. State Med.*, 43, 709 (1935).

Because of selective reflection of various spectral regions, consideration must be given to the nature of the reflectors used with either the carbon or the mercury arc. These, if improperly chosen, may alter the quality of the radiant energy emitted by the source. If it is desired to study the relative effectiveness of various spectral regions, provision must be made for the use of suitable filters surrounding the source to isolate various bands of wave lengths.

The intensity on a given skin surface normal to the rays varies approximately as the inverse square of the distance from the arc. This is only a rough statement because the arcs used are not true point-sources of light. The intensity also varies with the cosine of the angle made by the skin surface with the beam of radiant energy. These factors may be considered in calculating the amounts of energy received per square cm. of skin from known values of the energy output of the source under the conditions of operation employed. In practice, however, the energy incident upon the patient may be directly measured by some calibrated apparatus, such as a thermocouple, photoelectric cell, or chemical actinometer.

In determining the dosage in practical therapy, the physician is usually guided, not so much by energy measurements, as by experience with the effects of the source on patients with various types of skin. A test exposure is made to determine the time required to produce a given degree of erythema, and on this is based the dosage to be applied to the body. The erythema test is made on the patient's upper arm, which is covered by a shield cut from a large envelope and containing five small holes. Under this shield is placed a strip of the same material as the shield, which may be withdrawn so as to expose successive areas. A convenient series of exposures permits the irradiation of the areas for times successively doubled from fifteen seconds in the last exposed area to a total of four minutes in the first. These periods are usually suitable for exposures at 36 inches from a bare A-2 National Carbon Co. carbon arc with high-intensity carbons and without a filter glass. In an individual of less than average susceptibility to sunburn, the spot receiving the four-minute exposure shows a visible degree of erythema about forty minutes after the completion of the test and all five spots are clearly visible in less than two hours. Substantial pigmentation results from all exposures but that of fifteen seconds. With the filter glass in place the exposure period required to produce a given degree of erythema is three to four times as long as that required when the same carbons are used without the filter. This method of grading the dosage serves as a safeguard against overexposing areas large enough to cause painful and possibly injurious burns.

The full line curves of Figure 21 (p. 61) show the distance at which the radiation intensity in the wave-length region 2900 to 3100A. equals that found in average clinical sunlight for patients at various distances and angles from the filtered carbon arc. The average intensity of that wave-length band in clinical sunlight is taken as 14.5 microwatts per sq. cm. The curves are for high-intensity Sunshine carbons. With high-intensity therapeutic "C" carbons, the intensity will be over three times the value indicated in the figure. With the filter removed, the intensity of radiations shorter than 3100A will be about 18 times the values shown. The wave-length range specified was chosen for reasons which will become apparent in the discussion of the treatment of rickets in the following chapter.

Several clinicians attempt, in administering general irradiations for systemic effects, to produce a gradual deep tanning of the entire body without causing vesication or undue peeling of the skin. It is scarcely necessary to state that the eyes should be carefully protected during the exposures. Details of the technic should be sought in the detailed reports in the medical literature. It is sound practice to commence by fractional exposures, at each sitting exposing a fresh part and increasing the exposure of previously irradiated regions until the irradiations cover the whole body. This has been the practice of Rollier in heliotherapy, and it finds experimental justification in the work of Levy (1916) and of Gassul (1920), who have shown that general irradiation of the whole body at the first sitting may lead to unfortunate results. Although at one time it was suggested that patients could be sensitized to light to make the treatments more effective by the injection of eosin, such methods are no longer employed.[9]

MacCormac and McCrae[10] have given an account of a serious dermatitis which followed a mercury-arc irradiation of about an hour and ten minutes in the case of a patient who fell asleep during his customary artificial sunbath. After a severe sunburn, there resulted ten days later a severe toxic generalized dermatitis and recovery was delayed for over a month.

There is as yet no general agreement as to the best methods of conducting irradiation therapy. Details of the methods employed and of the results obtained in the treatment of tuberculosis of the bones and joints, peritoneum, intestines, lymph-nodes and genito-urinary system must be sought in the texts of Rollier,[11] of Mayer,[12] and of Russell and Russell,[13] which deal with the experience with this therapy in France, the United States and in England.[14]

There has been one group of workers which holds that pigmentation is necessary to the curative action of ultraviolet rays and that its degree may be regarded as an index of the progress of the cure. A filtering action of the pigment might serve to lessen the lethal action of exposures to intense sunlight at high altitudes where there may be available a very narrow band of radiations of wave-lengths between 2970 and 2910A. However, since most of the pigment is located in the basal cells of the epithelium, and the lethal action occurs in the prickle cells, the pigment could be expected to exert a protective action only upon the deeper tissues which, except in the case of the most intense irradiations, are comparatively slightly affected.

Balderrey and Ewald[15] stated that pigmentation is not merely a protection against the harmful effects of the shortest wave-lengths, but is an important factor in aiding the absorption of visible light, since its presence lessens the reflection from the skin. It also was suggested that the pigmented surface radiates heat at a slightly increased rate and so permits the body to be subjected to longer periods of irradiation without the production of symptoms of insolation.

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[9] György, P., and Gottlieb, K., *Klin. Wochschr.*, **2**, 1302 (1923); *Chem. Abs.*, **19**, 1600 (1925).

[10] MacCormac, H., and McCrae, H. M., *British Med. J.*, **I**, 693 (1925)

[11] Rollier, A., "Heliotherapy." Translated by de Swietochowski, H. Milford, Oxford University Press, 1927.

[12] Mayer, E., "Clinical Application of Sunlight and Artificial Radiation," Baltimore, Williams and Wilkins Company, 1926.

[13] Russell, E. H., and Russell, W. K., "Ultraviolet Radiation and Actinotherapy," New York, Wm. Wood, 1928.

[14] For more recent reports, see Petter, C. K., *Ann Internal Med.*, **4**, 1452 (1931); Lehman, A. M., and Bartholomew, D. C., *J. Am. Med. Assoc.*, **98**, 1343 (1932); Willis, H. S., and Cohen, J., *Am. Rev. Tuberculosis*, **23**, 286 (1931); Jessel, G., *Lancet*, **I**, 1182 (1931), Pardee, K., *J. Bone & Joint Surgery*, **12**, 270 (1930); Cox, G. L., *Brit. J. Tuberculosis*, **24**, 1 (1930); *Tubercle*, **12**, 17 (1930); Phelps, W. M., *J. Bone and Joint Surgery*, **12**, 253 (1930); Mayer, E., *Ann. Internal Med.*, **11**, 1856 (1938).

[15] Balderrey, F. C., and Ewald, E., *Am. Rev. Tuberculosis*, **8**, 501 (1924).

One school maintains that pigmentation may be produced without visible erythema, provided very carefully graduated doses are employed. Another believes that in the treatment of tuberculosis, doses causing erythema are more productive of beneficial results than are repeated smaller ones. If the views of those who believe the beneficial effects are to be ascribed to the non-specific proteins or protein decomposition products produced by injured cells are held correct, it might be thought necessary to use wave-lengths capable[16] of producing erythema in order to produce the necessary cell injury. If, on the other hand, the beneficial results are due to the formation in the skin of some substance with curative properties, as has from time to time been suggested in analogy with the mechanism of the cure of rickets, then it is conceivable that wave-lengths other than those which cause erythema might suffice. These speculations state problems for the future which will probably best find their solution in well-controlled experiments in large institutions. It would be possible from such experiments to learn definitely which wave-lengths are essential to the curative process and to determine with some degree of accuracy the dosages of energy required at these wave-lengths. Such information would provide a basis for a study of the mechanism by which the therapeutic results are attained—a mechanism regarding which we have at present little more than speculations.

Phelps[17] has asserted that the beneficial results are due to a band of radiant energy lying between 3200 and 3800A. His work could not, however, be corroborated by Luce-Clausen and Bayne-Jones[18] and it has been suggested that his assumption that the sunlight he employed was devoid of rays shorter than 3130A may have been erroneous and that the filters he employed in other experiments may not have completely eliminated the shorter wave-lengths.

Experiments in which guinea pigs were injected intra-abdominally with tubercle bacilli failed in most cases to indicate that irradiated animals were more resistant than the non-irradiated controls.[19] Greenfield[20] found some favorable response in the case of irradiations by direct sunlight in such experiments.

The possibility that the production of vitamin D has a favorable effect on tuberculosis will be considered in the following chapters. As yet opinions are divergent as to the advisability of employing this form of therapy in pulmonary tuberculosis. There is still an opinion held by such workers as Rollier and many others that phototherapy is dangerous in such cases. On the other hand, several recent observers including Potter, Eberson, Cooper and others believe that if caution is used, the treatment may be productive of valuable results.

Jemma[21] states that in twenty children with bone and joint tuberculosis, a lowered alkaline reserve was restored to normal during ultraviolet light therapy. In adult patients, Spence[22] observed a considerable rise in the blood cholesterol after a month of treatment. The greatest rise occurred in those patients who

[16] Peskind, S., *cf.* "Photochemical Immunization: Autogenous Vaccination Through Irradiation," S. P. Mount & Co., Cleveland, 1934.

[17] Phelps, W. M., *J. Bone and Joint Surgery*, **12**, 253 (1930).

[18] Luce-Clausen, E. M., and Bayne-Jones, S., *Am. Review Tuberculosis*, **24**, 686 (1931).

[19] Steinbach, M. M., Hess, A. F., and Weinstock, M., *Am. Rev. Tuberculosis*, **22**, 35 (1931).

[20] Greenfield, M., *Am. Rev. Tuberculosis*, **24**, 695 (1931).

[21] Jemma, G., *Pediatria Revista*, **36**, 878 (1928); *Chem. Abs.*, **22**, 4620 (1928).

[22] Spence, C., *Brit. J. Actinotherapy*, **3**, 148 (1928); *Chem. Abs.*, **23**, 858 (1929).

showed clinically the greatest improvement. No significant changes in the calcium and phosphorus levels were observed.

With the demonstration of the value of ultraviolet therapy in the treatment of tuberculosis and of rickets (see Chapter 38), irradiation came to be used with varying results in a wide variety of diseases. The literature is replete with claims for its efficacy in conditions ranging from mental diseases through whooping cough to bronchial asthma. Unfortunately, the results obtained have not been such as to sustain the enthusiasm with which the method was lauded. Illogical attempts to utilize ultraviolet light for conditions for which there is little theoretical or experimental foundation met with failure and caused many physicians to discard expensive equipment.

The physiological studies reviewed in the preceding chapter reveal few responses to ultraviolet light which may serve as a basis upon which to build a rational therapy. Studies of the irradiation of abnormal or diseased subjects have given, at least in the case of rickets, more promising results. It might be thought that the reduction in blood pressure to which reference has been made in the preceding chapter might serve as a basis for expecting irradiation to give results in the treatment of hypertension. Indeed, some favorable responses to this treatment were recorded by Laurens in a study of a series of cases of essential hypertension. Others, however, proved entirely refractory. Marx[23] reported rather favorable results in a series of 21 ambulant, hypertension patients, using carbon filament lamps. With the carbon arc, Bach[24] found that in 105 observations on 19 men and 10 women, the blood pressure fell during irradiation in 101, showed no change in 2 and increased slightly in 2 observations. The decreases averaged 7.2 mm; the largest was 17 mm. With the quartz mercury arc, Koenigsfeld[25] observed decreases of from two to eight mm. immediately after irradiation. In eclampsia, Hochenbichler[26] obtained marked decreases in blood pressure, but frequently it rose again shortly after the treatment. The probability is that dilatation of the skin vessels produces a transient lowering of the blood pressure and causes some decongestion of blood from the internal organs.

The results in anemias have not in general been encouraging, although some favorable results in pernicious anemia were reported from the Taft Heliotherapy Ward at the Cincinnati General Hospital.[27]

There is a widespread impression that the employment of ultraviolet light in treating patients with diabetes is dangerous. This is in part based upon observation by Sampson[28] and by McCaskey.[29] From the fact, however, that the blood sugar is commonly reduced somewhat during irradiation, it seems that there is little if any foundation for this contention. Indeed, some workers, such as Faber and Bloch,[30] have obtained encouraging results in its use in the treatment of diabetic children. Grayzel, Collens and McKenzie[31] found it to have no effect on the sugar balance of such patients.

That ultraviolet irradiation should increase the resistance of the skin to infection was a natural suggestion from the results of local therapy. Rollier noted that the eruptions of chicken pox are slighter than usual in patients with pigmented skin. Hyde and LoGrasso found that skin infections occurred but rarely in pigmented patients, and Carnot, Camus and Benard found that in rabbits irradiated before inoculation with vaccine virus, the development of an eruption was prevented.[82]

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[23] Marx, H., *Klin. Wochschr.*, **7**, 795 (1928).
[24] Bach, H., *Deut. Med. Wochschr.*, **37**, 401 (1911).
[25] Koenigsfeld, H., *Z. Klin. Med.*, **91**, 159 (1921).
[26] Hochenbichler, A., *Centralbl. Gynäkol.*, **51**, 1649 (1927).
[27] Friedlander, A., and Wiedemer, C., *Arch. Internal Med.*, **44**, 209 (1929).
[28] Sampson, C. M., "Physiotherapy Technique," C. V. Mosby, St. Louis, 1923.
[29] McCaskey, D., *New York Med. J.*, **109**, 504 (1919).
[30] Faber, F., and Bloch, C. E., *Am. J. Diseases of Children*, **30**, 504 (1925).
[31] Grayzel, H. G., Collens, W. S., and McKenzie, M. R., *Am. J. Diseases of Children*, **38**, 513 (1929).

That the blood should also become increasingly bactericidal as a result of the generalized irradiation of a patient has been occasionally suggested. Colebrook, Eidinow and Hill [83] have given some evidence for a temporary increase in the bactericidal power of the blood following a single exposure to the mercury arc. Robertson [84] believed that solar or mercury-arc irradiation of rats raised their resistance to infection with *B. coli communis*. Blasi [85] found that the opsonic index of the blood serum of children with a positive von Pirquet test toward the tubercle bacillus was increased after ten irradiations with the mercury arc. Hansen found that carbon arc baths applied to 230 patients who had received single injections of dead typhoid bacilli increased the formation of agglutinins in their blood. He believed the effect due to the heat of the deeply penetrating infrared rays. In general, however, immunological experiments (described in the preceding chapter) have given little foundation for a belief that irradiation increases resistance.

Many have suggested that generalized irradiations might protect people from the common cold. Maughan and Smiley at Cornell [86] conducted a series of experiments on students, in which 23 received full mercury-arc treatments at 30 inches, the arc being operated at 4 amperes and 130 volts. The entire posterior and anterior surfaces of the body received the rays for five minutes, the treatments being given weekly for about nine weeks. 58 controls were used. During this period the number of colds per individual treated was 1.48 and per individual untreated 2.48. These workers ascribed the failure of others to reduce the incidence of colds by this method to overdoses. In a second series, in one twelve-week period the results were 1.56 and 2.80 colds in the treated and untreated subjects. A second period of nine weeks showed 1.24 and 2.79, respectively. The subjects used were selected as being especially prone to suffer colds.

These results were, however, contradicted by the work of Doull, Hardy, Clark and Herman [87] who also used mercury arcs and gave light or moderate doses which produced only a minimal erythema. The total incidence was found to be slightly higher in the irradiated patients receiving more than ten treatments than in the controls. The cases occurring in the irradiated group also appeared to be somewhat more severe than those in the non-irradiated subjects.

Barenberg, Friedman and Green,[88] found that irradiation did not protect infants from whooping cough, chicken pox or respiratory infections. Both the carbon arc and the mercury arc were used. In children the evidence from blood counts showed, according to Gonce and Kassowitz [89] no enhanced bactericidal property in the blood after ultraviolet irradiation. They concluded that in the majority of their patients, particularly if they were the hosts of an infection, daily quartz lamp irradiation led to a lowered bactericidal power of the blood. The opposite effect was obtained in a few cases. Similar observations are due to Colebrook.[40] Hardy and Chapman, who studied the effect of irradiation on the ability of rabbits to resist *Bacillus leptisccpticum*, found light doses to have little effect and heavy doses to be harmful. According to Petrie,[41] the susceptibility of guinea pigs to spontaneous pneumococcus infection was not affected by irradiation. Negative results were also reported by Hill, Greenwood and Topley [42] in an extensive experiment on the effects of exposure under normal conditions on the resistance of over a thousand mice to *Pasteurella* infection.

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[82] See also Rivers, T. M., Stephens, H., and Gates, F. L., *J. Exptl. Med.*, 47, 37, 45 (1928).

[83] Colebrook, L., Eidinow, A., and Hill, L., *Brit. J. Exptl. Path.*, 5, 54 (1924); Eidinow, A., *Lancet*, II, 963 (1927); *Med. J. and Record*, 130, 695 (1929).

[84] Robertson, E. C., *Can. Med. Assoc. J.*, 19, 154 (1928); Robertson, E. C., and Ross, J. R., *Proc. Soc. Exptl. Biol. Med.*, 27, 999 (1930).

[85] Blasi, D., *Clinica Pediatrica*, 11, 832 (1929).

[86] Maughan, G. H., and Smiley, D. E., *J. Preventive Med.*, 2, 69 (1928); *Am. J. Hygiene*, 9, 466 (1929).

[87] Doull, J. A., Hardy, M., Clark, J. H., and Herman, N. B., *Am. J. Hygiene*, 13, 460 (1931).

[88] Barenberg, L. H., Friedman, I., and Green, D., *J. Am. Med. Assoc.*, 87, 1114 (1926); Barenberg, L. H., and Lewis, J. M., *Ibid.*, 90, 504 (1928).

[89] Gonce, J. F., and Kassowitz, K., *J. Am. Med. Assoc.*, 90, 280 (1928).

In the annual report of the Medical Research Council of London for 1927-8, it is stated that heavy expenditures for Vita-glass or other ultraviolet-transmitting glasses for school rooms or for expensive irradiation equipment for schools has not been justified. Under the auspices of the Council, Dr. Dora Colebrook arranged an elaborate test of the value of lamp therapy, the results of which were entirely negative. Her experiment, however, has been criticized, notably by Hill and Laurie,[43] who felt that the control children had been unwisely selected in that they lived in a district where the hygienic conditions and the available sunlight had been adequate. Their own observations indicated that irradiation improved the appetite and sleep of a group of children. The Council on Physical Therapy of the American Medical Association has stated that as far as normal persons are concerned the claim that exposure to ultraviolet rays increases or improves the tone of the tissues or of the body as a whole, stimulates metabolism or tends to prevent colds has not been conclusively substantiated.

Thus it would seem that opinions are still divergent in regard to the value of generalized irradiations on the general health and resistance to disease. This is a particularly difficult subject to investigate objectively. General reports of feelings of exhilaration or invigoration cannot be appraised scientifically. In contrast to this, the value of irradiation on the prevention of rickets is definitely confirmed and well understood.

There is some evidence that irradiation has a beneficial effect in bronchial asthma, at least in children.[44] In hay fever, hyperesthetic rhinitis and the asthmas, investigations by Novak and Hollaender [45] indicated favorable results attributed to an influence exerted upon the blood calcium which tended to be low in these conditions. Favorable effects of ultraviolet therapy given in conjunction with calcium salts in epilepsy have been reported by Borrows.[46]

Roskin and Romanova [47] find that non-therapeutic doses of novarsolan given with ultraviolet irradiations have no effect on malaria in canaries although they are effective in mice. The serum of irradiated mice has the property of increasing the therapeutic action of novarsolan, neoarsphenamine and novarsenol in the malaria of canaries, presumably because of the passive transfer of some necessary factor. Although Roskin and others claimed [48] that irradiation synergizes the trypanocidal action of neoarsphenamine, Giemsma and Ellenbogen [49] could not confirm such an action. Negative results have also been reported for the effects of ultraviolet irradiation on the splenic anemia of kala-azar by Morabito,[50] although in the anemias of luetic or tuberculous origin the results were more favorable.

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[40] Colebrook, L., *Brit. Med. J.*, **2**, 11 (1924).

[41] Petrie, G. F., *J. Hygiene,* **30**, 154 (1930-31).

[42] Hill, L., Greenwood, M., and Topley, W., *Brit. J. Exptl Path.*, **11**, 182 (1930).

[43] Hill, L., and Laurie, A. R., *Lancet,* **I**, 182 (1931).

[44] Saidman, J., *Arch. Med-Chir. l'App Respiratoire,* **3**, 480 (1929).

[45] Novak, F. J., and Hollaender, A. R., *J. Am. Med. Assoc.*, **81**, 2003 (1923); *Chem. Abs.*, **18**, 1153 (1924).

[46] Borrows, P. J., *U. S. Veterans Bureau Med Bull.*, **7**, 661 (1931); *Chem. Abs*, **26**, 2245 (1932)

[47] Roskin, G., and Romanova, K., *Z. Immunitats.*, **82**, 461 (1934); *Chem. Abs.*, **28**, 7361 (1934); *Z. Immunitäts.*, **62**, 147, 158 (1929); **72**, 445 (1931); **67**, 94 (1930); *Chem. Abs.*, **25**, 3080 (1931).

[48] Roskin, G., Bichowskaja, A., and Schischliaiewa, S., *Z. Immunitäts.*, **67**, 91 (1930); Roskin, G., *Ibid.* **69**, 240, 473 (1930); **63**, 452 (1929); *Chem. Abs.*, **25**, 3080 (1931).

[49] Giemsma, G., and Ellenbogen, V., *Z. Immunitäts.*, **67**, 78 (1930); *Chem. Abs.*, **25**, 3080 (1931); positive results have been reported by Marzinovskii, E. J., *Z. Immunitäts.*, **74**, 379 (1932) and by Orlov, S., and Levinson, L., *Ibid.*, **78**, 264 (1933); *Chem. Abs.*, **27**, 5422 (1933).

Attempts have been made to treat mastitis in cows by ultraviolet irradiations; but Gildow, Hansen and Cherrington[51] found no consistent reduction in the number of bacteria or of the leucocytes in the middle milk of cows with subacute or chronic mastitis after such treatment. Ultraviolet treatment has also been proposed for distemper in dogs.[52]

Von Fellenberg[53] was unable to obtain evidence that ultraviolet irradiation had any effect upon endemic goiter. The weight and the iodine content of the thyroid are the same in rats reared in direct sunlight and in those reared in darkness.[54] Smith,[55] however, believes that a lack of sunlight may result in a deficiency of iodine in the thyroid gland and notes a relationship between a lack of irradiation and endemic goiter in the United States, India and New Zealand. In the last-named region the iodine content of the soil seems to be proportional to the solar radiations and similar observations have been made in regard to variations in the iodine content of potatoes grown in South Carolina.

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[50] Morabito, F., *Pediatria Revista*, **35**, 1112 (1927); *Chem. Abs.*, **22**, 1801 (1928).

[51] Gildow, E. M., Hansen, H. C., and Cherrington, V. A., *J. Am. Vet. Med. Assoc.*, **35**, 55 (1933); *Chem. Abs.*, **27**, 1399 (1933).

[52] For other applications in veterinary medicine, see Patton, J. W., *J. Am. Veterinary Med.*, **69**, 734 (1926).

[53] Von Fellenberg, T., *Biochem. Z.*, **235**, 205 (1935).

[54] But see Bergfeld, W., *Endokrinologie*, **6**, 269 (1930); *Chem. Abs.*, **24**, 3552 (1930).

[55] Smith, J. H., *Arch. Internal Med.*, **50**, 76 (1932).

Chapter 38

Rickets and Irradiation

Rickets is a common disease of infants and young children. It consists chiefly in a faulty deposition of calcium in the extremities of the long bones. The clinical picture is thoroughly discussed in a book by Hess[1] which also includes a critical discussion of the flood of papers which appeared subsequent to 1919 regarding the importance of vitamin D in this condition and the relation of sunlight to the production of this vitamin in the skin. The disease is accompanied by disturbances in calcium or phosphorous metabolism. It is usually characterized by low values of either or both calcium and phosphorus in the blood serum.

In 1909, the pathological studies of Schmorl[2] brought to light an interesting seasonal variation in the incidence of the disease. There is a high incidence of rickets in winter and the healing of the disease, slight in winter, reaches its maximum in summer. Not for some time, however, were attempts made to correlate these data with the seasonal variations of the intensity of sunlight, although it is true that an Englishman, Palm, had suggested as early as 1890[3] that the chemical activity of the sun's rays may play an important part in the therapy of this disease. An experiment by Raczynski[4] attracted little attention. He kept one puppy in sunlight and another of the same litter in darkness for six weeks. At the end of this period, the body of the first was found to contain much more calcium and phosphorus than did that of the second. Bernhard in 1917 also drew some conclusions as to the influence of sunlight on the incidence of rickets in the children of certain Alpine villages.

Apparently the first definite statement that the irradiation of a rachitic child with ultraviolet rays would bring about a cure was published by Huldschinsky in 1919.[5] His paper contained a number of Rontgenograms which indicated beyond any doubt that the epiphyses of the long bones of rachitic infants undergo rapid calcification following the exposure of their bodies to a mercury-vapor lamp.

Clinical observations by Hess and Unger a year previously had indicated that such irradiations might have a slight effect in decreasing the size of the enlarged costo-chondral junctions, the so-called rachitic rosary, a diagnostic sign of rickets. They attached little significance to this, however, for in 1920 they stated that children in glass cubicles receiving a liberal supply of light nevertheless became rachitic and were not benefited by ultraviolet light treatments.[6] A year later, however, they published a preliminary note on the cure of rickets by sunlight[7] in which they employed the expression "encouraged by our results in curing rickets by means of the ultraviolet ray." At this time they also attributed the seasonal

[1] Hess, A. F., "Rickets, Osteomalacia and Tetany," Philadelphia, Lea and Febinger, 1929.

[2] Schmorl, G., *Ergeb. der Inn. Med. u. Kinderheilk,* 4, 403 (1909); cited in Hess, A. F., "Rickets, Osteomalacia and Tetany," Philadelphia, Lea and Febinger, 1929.

[3] Palm, T. A., *Practitioner,* 45, 270, 321 (1890).

[4] Raczynski, J., *Compt rend. assoc. intern. pediat.,* 308 (1912); cited in Hess, A. F., "Rickets, Osteomalacia and Tetany," Philadelphia, Lea and Febinger, 1929.

[5] Huldschinsky, K., *Deut. Med. Wochschr.,* 45, 712 (1919).

[6] Hess, A. F., and Unger, L. J., *J. Am. Med. Assoc.,* 74, 217 (1920).

[7] Hess, A. F., and Unger, L. J., *J. Am. Med. Assoc.,* 77, 39 (1921)

variations in the incidence of the disease to the seasonal variations in the intensity of sunlight.[8]

The further study of this disease was promoted by the discovery that it could be produced in experimental animals by the use of deficient diets, particularly those low in phosphorus.[9] It was soon shown that animals receiving a diet either low in phosphorus and high in calcium or one low in calcium and high in phosphorus developed symptoms of rickets. They could be protected from the effects of the diet by daily exposures to sunshine of only fifteen minutes, except in winter when longer exposures were required. The demonstration that light filtered through a window of ordinary glass was ineffective showed that only the ultraviolet portion of the solar spectrum was important. Only short periods of exposure to ultraviolet sources were required for protection against the defective diets. With the quartz mercury lamp a daily irradiation of three minutes at a distance of three feet was adequate. These effects on the growth and skeletal calcification of the rats were similar to, if not identical with, those brought about by sunshine or by the addition of cod-liver oil to the diet. Cod-liver oil was the remedy in most frequent use in the treatment of rickets.[10]

These results were quickly confirmed on many sides [11] and the curative results of carbon-arc treatments also were observed.[12] During the treatment the inorganic phosphates of the blood increased, and the signs of the disease subsided. Preadministration of phosphates hastened the cure, although addition of dipotassium hydrogen phosphate in the absence of irradiation was unsuccessful in clinical cases.

The next important advance was the demonstration that the light acts by a chemical mechanism. Hess and Weinstock [13] showed that a section of excised human skin after irradiation by a mercury arc when fed to rats, protected them from a deficient diet, although similar amounts of nonirradiated skin were ineffective. It was thus obvious that an antirachitic substance had been formed photochemically in the irradiated skin. This was later confirmed by Falkenheim,[14] who also showed that the irradiation of but one portion of the skin of a rat produces antirachitic properties in other portions of the skin, although to a less extent than in the directly irradiated area. This observation implied that some of the active agent produced in the skin may be absorbed by the blood and distributed to other portions of the skin. As late as 1926, however, Bloch and Faber [15] denied the existence of the hypothetical antirachitic material, although they admitted that ultraviolet light had a curative action on the disease. Hume, Lucas and Smith [16] showed that normal calcification could be produced in rachitic rabbits by irradiating an area of skin as small as 2.5 by 3.5 cm. for only ten minutes three times a week, a proof of the extraordinary effectiveness of the unknown material formed in the skin.

It has been stated that cod-liver oil had been known for some time to contain a substance exerting a similar curative effect upon rickets and the question naturally arose as to whether this might be identical with the material formed during the irradiation of skin. For several years it had been recognized, in large part because of the work of Mellanby, that cod-liver oil contains fat-soluble vitamins essential to the normal development of animals. But for a time it was not recognized that there are at least two fat-soluble vitamins in cod-liver oil. The investigations by which it was established that one of these, vitamin A, is concerned primarily with growth and the prevention of xerophthalmia, and that another, vitamin D, is concerned with the prevention of rickets, lie for the most part beyond the scope of our subject matter.

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[8] Hess, A. F., and Unger, L. J., *Am. J. Diseases of Children*, **22**, 186 (1921).

[9] Hess, A. F., Unger, L. J., and Pappenheimer, A. M., *J. Biol. Chem.*, **50**, 77 (1922); *J. Exptl. Med.*, **36**, 437 (1922); Hess, A. F., and Gutman, M. B., *J. Am. Med. Assoc.*, **78**, 29 (1922).

[10] Powers, G. F., Park, E. A., Shipley, P. G., McCollum, E. V., and Simmonds, N., *Proc. Soc. Exptl. Biol. Med.*, **19**, 120 (1921).

[11] Schultzer, P., and Sonne, C., *Acta Med. Skand., Suppl.*, **VII**, 97 (1924); Eckstein, A., *Arch. Kinderheilk.*, **74**, 1 (1924); *Chem. Abs.*, **18**, 3207 (1924).

[12] Hess, A. F., and Unger, L. J., *J. Am. Med. Assoc.*, **78**, 1596 (1922).

[13] Hess, A. F., and Weinstock, M., *J. Am. Med. Assoc.*, **80**, 687 (1922).

[14] Falkenheim, C., *Klin. Wochschr.*, **5**, 2071 (1926).

[15] Bloch, C. E., and Faber, F., *Am. J. Diseases Children*, **30**, 504 (1926).

[16] Hume, E. M., Lucas, N. S., and Smith, H. H., *Biochem. J.*, **21**, 362 (1927).

As early as 1922, Hume[17] showed that rats on a vitamin A-deficient diet could not be protected from the effects of the lack of this vitamin by irradiation if the experiment was continued for a sufficient period. It followed that this vitamin is not produced in the animal as a result of photochemical processes. This was also the conclusion of Goldblatt and Soames[18] from independent experiments. Sheets and Funk[19] similarly found that on a diet deficient in fat-soluble vitamins (then called incorrectly vitamin A) a three- to five-minute daily irradiation by ultraviolet light prevented the appearance of rickets and, although the rate of growth of the animals was normal, xerophthalmia developed. Powers, Park and Simmonds[20] clearly recognized the existence of two separate factors or vitamins in cod-liver oil, the antixerophthalmic A and the antirachitic D.

It was next shown by Goldblatt and Soames[21] that so long as the necessary vitamins are supplied in the diet light is not essential. Other experiments prior to the recognition of vitamins A and D as separate entities were by Eckstein[22]

Steenbock and Nelson[23] found that such antirachitic agents as ultraviolet rays or cod-liver oil would restore the growth of rats maintained on a diet deficient in the fat-soluble vitamins but would not postpone the onset of xerophthalmia. They viewed these results as supporting the view that cod-liver oil contains two vitamins. It was also shown that non-irradiated rats receiving a diet deficient in the antirachitic factor showed normal growth when placed in the same cage with irradiated rats on the same diet. The same effect was obtained when the rats were placed in a jar on a galvanized iron wire screen contaminated slightly by other rats having been kept on them and then irradiated. It was necessary that the rats have access to the irradiated screen in order that they might ingest traces of excreta or skin secretions which had been irradiated. Irradiated air had no beneficial effects.[24]

EFFECTIVE WAVE-LENGTH REGIONS

Once the effects of ultraviolet light in preventing the development of rickets had been established, the physical aspects of the process were studied to learn more precisely which wave-lengths are effective. Pappenheimer and Weinstock,[25] by interposing standard glass filters, found that wave-lengths as long as 3340A had no protective action, the effective rays being in the neighborhood of 3130A. Hess and Weinstock[26] thought the wave-length must not be longer than 3130A and found the effectiveness of the 3020A line very great. Mouriquand, Bernheim and

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[17] Hume, E. M., *Lancet*, **II**, 1318 (1922).

[18] Goldblatt, H., and Soames, K. M., *Lancet*, **II**, 1321 (1922).

[19] Sheets, O., and Funk, C., *Proc. Soc. Exptl. Biol. Med.*, **20**, 80 (1922); *Chem. Abs.*, **17**, 3528 (1923).

[20] Powers, G. F., Park, E A., and Simmonds, N., *Proc Soc Exptl Biol. Med*, **20**, 81 (1922).

[21] Goldblatt, H., and Soames, K. M., *Biochem. J.*, **17**, 294, 622 (1923).

[22] Eckstein, A., *Arch. Kinderheilk*, **73**, 1 (1923); Allenbach and Simon, R., *Rev. Hyg. Soc. Strasburg*, **81**, 670 (1923); *Bull. Soc. Hyg. Aliment*, **11**, 124 (1923); *Chem Abs.*, **17**, 2306 (1923).

[23] Steenbock, H., and Nelson, M. T., *J. Biol. Chem.*, **56**, 355 (1923); see also *Ibid.*, **62**, 575 (1925) and Steenbock, H., Nelson, M. T., and Black, A., *Ibid.*, **62**, 275 (1924).

[24] For further discussion of the separate assay of vitamins A and D on rats see Dutcher, R. A., and Kruger, J. H., *J. Biol. Chem.*, **69**, 277 (1926) and Sherman, H. C., and Hessler, M. C., *J. Biol. Chem.*, **73**, 113 (1927).

Theobalt[27] observed that rats irradiated five minutes daily by a mercury arc with an interposed Wood's glass filter developed rickets, but that those receiving 90 minutes of irradiation under these conditions did not. Luce[28] found that a filter transmitting 5 per cent of the incident light at 3050A and cutting off completely at 2960A destroyed the effectiveness of irradiation, but that a screen transmitting 80 per cent at 3000A and letting through some rays to 2400A, and one transmitting 77 per cent at 3000A and cutting off between 2650 and 2450A, each transmitted the effective rays. Hess and Weinstock[29] believed that wave-lengths shorter than those available in sunlight had even greater potency. They noted during the winter months when the shorter wave-lengths do not reach the earth, and even the longer ones reach it with lowered intensity, that the effective wave-lengths available are reduced to a band only about 50A wide, between 3130 and 3080A. Maughan[30] found the wave-length 2968A four times as effective as 3020A.

Huldschinsky[31] once proposed to term rays of wave-length longer than 3200A, ultraviolet A, those between 3200 and 2890A ultraviolet B (standing for biologically active), and those shorter than 2890A, ultraviolet C. This suggestion failed to find general favor.

Bunker and Harris[32] advocated an attitude of caution in regard to the acceptance of the view that only a narrow band near 3000A is of importance.

AMOUNTS OF ENERGY REQUIRED

Recent studies indicate that the most effective wave-length for curing rickets in rats is 2804A.[33] To produce healing equivalent to that due to one international unit of vitamin D, the following energies (in thousands of ergs) were required at various wave-lengths: 2653A, 287; 2804A, 226; 2894A, 395; 2967A, 280; 3024A, 553; 3128A, 27,545. Prolonged irradiation, particularly by the shorter wave-lengths 2653, 2804 and 2894A has a destructive action. Stein and Lewis[34] found that at Denver, direct sunlight in June and July was effective for rats in exposures as short as 3.75 minutes daily. Curative effects are produced in either chickens or human infants by irradiation by even, in some cases, tungsten filament lamps in thin Corex D glass bulbs, according to Maughan and Dye,[35] and Gerstenberger and Horesh.[36] In the case of the children, continuous exposures were given for twelve hours to two lamps six feet apart housed in oxidized aluminum reflectors five and a half feet above the bed level. Hauch and Hanke[37] found that February sunlight at the street level in Chicago failed to protect rats on a rachitic diet and exposed behind commercial ultraviolet glasses. Under the same conditions, however, they were protected fully by March to April sunlight. Control rats behind ordinary glass were not protected.

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[25] Pappenheimer, A. M., and Weinstock, M., *Proc. Exptl. Biol. Med.*, **20**, 14 (1922).

[26] Hess, A. F., and Weinstock, M., *J. Am Med. Assoc.*, **80**, 687 (1922).

[27] Mouriquand, G., Bernheim, M., and Theobalt, Mlle., *Compt. rend.*, **182**, 1490 (1926).

[28] Luce, E. M., *J. Biol. Chem.*, **71**, 187 (1926).

[29] Hess, A. F., and Weinstock, M., *J. Am. Med. Assoc.*, **89**, 1222 (1927).

[30] Maughan, G. H., *Am. J Physiol.*, **87**, 381 (1928).

[31] Huldschinsky, K., *Klin. Wochschr.*, **5**, 1972 (1926).

[32] Bunker, J., and Harris, R., *Am. J. Public Health*, **20**, 1278 (1930).

[33] Knudson, A., and Benford, F., *J. Biol. Chem.*, **124**, 287 (1938).

[34] Stein, H. B., and Lewis, R. C., *Am. J. Diseases of Children*, **41**, 62 (1931).

[35] Maughan, G. H., and Dye, J. A., *J. Opt. Soc. Am.*, **20**, 279 (1930); *Proc. Soc. Exptl. Biol. Med.*, **28**, 106 (1930).

[36] Gerstenberger, H. J., and Horesh, A. J., *J. Am. Med. Assoc.*, **96**, 766 (1931).

[37] Hauch, J. T., and Hanke, M. E., *Ind. Eng. Chem.*, **23**, 1398 (1931).

In New Orleans, Mayerson and Laurens[38] found the following to be the minimal daily times of irradiation necessary: February and March, 3 to 5 minutes for chicks and 5 to 6 minutes for rats. For either, the times were from April through October, 3 to 5 minutes, and from November through January, 5 to 6 minutes. The average daily amount of direct solar radiation of wave-length shorter than 3130A that will prevent rickets in rats is less than 0.001 calorie per sq. cm. from April to October, and between 0.001 and 0.002 calorie during the rest of the year. Of course, it is necessary to consider the number of sq. cm. exposed at such intensities since there is a minimal dose of vitamin D which must be produced in the total irradiated area for the protective action to become effective. For the prevention of leg weakness in chicks the amount of energy required was found to be about 0.00069 calorie per sq. cm. daily.

Children need have only a small portion of their bodies irradiated for successful results. Thus Catel[39] found it necessary to irradiate only the face or any area of 90 sq. cm.

There have been several other studies of the effectiveness of winter sunshine at various geographical locations. Tisdall and Brown,[40] working at Toronto, found that a marked increase in the antirachitic effect of sunshine occurs whenever the sun reaches an altitude of 35° or more. Geographically, rickets is uncommon or exists in but a mild form in those places where the minimal seasonal altitude of the sun is not below this angle, and severe rickets is chiefly encountered in those cities where the altitude is below that value for some months of the year. At Toronto, the antirachitic effect of the skyshine was about one-half to two-thirds as great as that of sunshine, by which is meant both the direct rays from the sun and the rays reflected from the sky and clouds. Even December skylight had a definite antirachritic effect. Fleming[41] found that at Washington, D. C., the winter sunlight is antirachitic for rats after passing through Vitaglass. Under the same conditions, north skylight was also protective during the months of April, May, June and July. At Boston, Wyman[42] found it possible to cure rickets in the winter months by exposures to sunlight through quartz windows or Corning glass windows, although the results were less favorable with Vitaglass. (See Chapter 10.) Favorable results were obtained also by means of Cel-O-Glass windows.[43] Jendrassik and Papp[44] found that at Budapest the sunlight was ineffective during December and January. Its activity then rose to a sharp and high peak at mid-June and declined again practically at the same rate.

A painstaking investigation of the energy required is that of Sonne and Rekling,[45] who employed a monochromator and determined by means of a thermopile the energy in gm. calories per sq. cm. incident at each of several wave-lengths on an area of the experimental animals of 8.1 sq. cms. In this way it was possible to eliminate the relative intensities of the various lines emitted by the source. The effect of the 3130A line was doubtful, although the incident energy amounted to $4.3\times0.708\times10^{4}$ gm. cal. per sq. cm. per minute. At 3020 to 2970A with a somewhat lower intensity ($3\times0.708\times10^{-4}$ gm. cal. per sq. cm. per minute) there was a strong antirachitic action. This was also the case at 2650A, although the intensity was lower, $1.5\times0.708\times10^{-4}$ gm. cal. It was also strong at 2530A where the intensity was slightly greater, $1.6\times0.708\times10^{-4}$ gm. cal. On the other hand, at 2480 and at 2390A where the energies were respectively 0.7 and $0.55\times0.708\times10^{-4}$ gm. cal. per sq. cm. per minute, there was but slight action. No protection was afforded by the wave-lengths 2270 to 2200A, with $0.4\times0.708\times10^{-4}$ gm. cal. per sq. cm. per minute.

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[38] Mayerson, H. S., and Laurens, H., *Am. J. Physiol.*, **102**, 422 (1932).

[39] Catel, W., *Monatschr. Kinderheilk.*, **54**, 426 (1932); *Chem. Abs.*, **27**, 2184 (1933).

[40] Tisdall, F. F., and Brown, A., *Can. Med. Assoc. J.*, **20**, 253 (1929); *Chem. Abs.*, **23**, 3007 (1929); *Am. J. Diseases of Children*, **34**, 721, 737, 742 (1927); **36**, 734 (1928); *J. Am. Med. Assoc.*, **92**, 860 (1929); **94**, 854 (1930).

[41] Fleming, W. D., *Military Surgeon*, **62**, 592 (1928); **63**, 658 (1928).

[42] Wyman, E. T., *Boston Med. & Surg. J.*, **197**, 376 (1927).

[43] Wyman, E. T., Drinker, P., and Mackenzie, K. H., *Am. J. Diseases of Children*, **39**, 969 (1930).

[44] Jendrassik, A., and Papp, S., *Biochem. Z.*, **268**, 364 (1934). In these experiments ergosterol rather than patients or experimental animals was irradiated.

[45] Sonne, C., and Rekling, E., *Strahlentherapie*, **25**, 552 (1927); cited by Laurens, H., "The Physiological Effects of Radiant Energy," New York, The Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1933.

The opinions of workers who have studied the influence of the pigment of the skin on the curative effects of sunlight differ somewhat. Schultzer and Sonne and Hess, and Unger and Pappenheimer believe that pigmentation in rats somewhat lessens the effects of irradiation. In children, however, Kramer, Casparis and Howland, as well as Levinsohn,[46] conclude that the skin pigment of the Negro child does not interfere with the action of ultraviolet rays.

Gerstenberger and Hartman[47] found that quartz lamp exposures weekly with doses of one erythema unit for negro infants, and less for white infants, applied to both front and back, caused healing in practically the same time as did heavier doses. Gerstenberger and Russell[48] obtained similar results with the General Electric Sunlamp S-1. Using a quartz lamp at 80 cm., Vollmer found a weekly dose of from four to five minutes each to the chest and back to be the minimal effective dose. Cures were effected after the application of about 100 minutes of treatment.

EFFECTS ON MINERAL METABOLISM.

Ultraviolet irradiation cannot overcome mineral deficiencies of the diet. Its function is to supply the vitamin D necessary to control the proper utilization of the calcium and phosphorus in the diet. Theiler[49] emphasized the fact that when the phosphorus of the diet of cattle is deficient rickets will develop in the presence of abundant solar radiations. Many papers have been devoted to the effects of irradiation upon the blood phosphorus and calcium levels during the cure of rickets. In contrast to the negative results discussed in the preceding chapter in regard to the influence of irradiation upon these values in the normal individual, there is general agreement that if the mineral contents of the diet are suitable, the low values which characterize rickets are readily restored to normal by irradiation or by the administration of vitamin D.

Kramer, Casparis and Howland[50] found values for the inorganic phosphorus in the serum of the blood of rachitic infants to vary from 2.7 to 3.2 mgm. per cent. Under quartz lamp treatment, this increased gradually to a maximum of 6 mgm. per cent, the normal value. Hess and Lundagen[51] observed a seasonal variation in the level of the inorganic phosphates of the blood corresponding to and determined by the seasonal variations in the ultraviolet energy of the available solar spectrum.

By 1923, it was[52] reported that the mean serum calcium content of normal infants from two months to ten years of age varies between 10 and 12 mgm. per 100 cc. In twenty rachitic infants, it ranged from 7.9 to 10.4 mgm. with an average of about 9.2. Two children of three and eight years with irreducible rachitic deformations had normal or slightly greater amounts of calcium, 11.8 and 11.4 mg. respectively. The calcium content of the serum is not modified by the injection of calcium chloride, but is altered by ultraviolet rays. After eight daily irradiations of thirty minutes each at 1.2 meters from a 1200 c.p. carbon arc given ten infants the serum calcium was decidedly increased in seven and after 24 irradiations it was well up to the normal value in eight of the children. The two infants which failed to show an increase in the calcium had dark skins. Orr, Holt, Wilkins and Boone[53] also showed that infants with active rickets are unable to retain calcium and phosphorus even though these elements are present in adequate amounts in the diet and that ultraviolet rays cause these elements to be retained. They observed that after irradiation increased amounts of these elements are found in the urine, indicative of an increased absorption of these essential minerals from the intestine. They argued that defective intestinal absorption in rickets is the cause of the low serum calcium and phosphorus, and is the ultimate cause of the defective calcification of the bones. That calcification at the junction of the bones and cartilage could be promoted by irradiation also was demonstrated radiographically by Vignard, Mouriquand, Chassard and Bernheim.[54]

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[46] Kramer, B., Casparis, H., and Howland, J., *Am. J. Diseases of Children*, **24**, 20 (1927); Levinsohn, S. A., *Ibid.*, **34**, 955 (1927).

[47] Gerstenberger H. J., and Hartman, J. I., *J. Am. Med Assoc.*, **92**, 367 (1929).

[48] Gerstenberger, H. J., and Russell, G. R., *J. Am. Med. Assoc.*, **94**, 1049 (1930); Vollmer, H., *Klin., Wochschr*, **9**, 2300 (1930).

[49] Theiler, A., *Veterinary J.*, **90**, 159 (1934); *Chem. Abs.*, **28**, 5503 (1934).

[50] Kramer, B., Casparis, H., and Howland, J., *Am. J. Diseases of Children*, **24**, 20 (1922).

[51] Hess, A. F., and Lundagen, M. A., *J. Am. Med. Assoc.*, **79**, 2210 (1922).

[52] Lesné, E., deGennes, L., and Guillaumin, *Compt. rend.*, **177**, 291 (1923); *Chem. Abs.*, **17**, 3540 (1923); see also Kramer, B., and Boone, F. H., *Proc. Soc. Biol. Exptl. Med.*, **20**, 87 (1922).

Clark[55] reported that the diffusible calcium of the serum, measured by dialysis in collodion sacks against physiological salt solution, may be increased by subjecting it to quartz mercury arc irradiations. The diffusible calcium in rabbit serum rose from 38 to 58% and in dog serum from 44 to 53%.

Hart, Steenbock and Elvehjem[56] induced experimentally negative calcium balances in mature lactating goats. Daily mercury arc irradiation changed these to positive and also appreciably increased the blood phosphorus. This was confirmed by Orr, Henderson and Magee,[57] who believed the results might be accounted for by a decreased elimination of calcium in the feces, the urinary excretion remaining practically constant. These results favored the view that irradiation induces an increased absorption of calcium from the intestines.

Schultzer[58] defines the Ca retention coefficient as the number of mg. retained per g. increase in body weight of rats during growth. The coefficient was 4.7 to 5.2 in young rats on a rachitic diet and with evident rickets. After irradiation, it was raised to 10. For phosphorus the values were 8.1 to 9.5 before and 15.7 after the cure of the rickets. Similar results also could be brought about by giving the rats cod-liver oil or, if the diet was deficient in phosphorus, by giving phosphates. A number of rachitic rats showed an average of 11.9 mgm. of calcium and 5.6 mgm. of phosphorus per 100 cc. of serum.[59]

In four ultraviolet-treated rats the serum calcium rose to 15.2 and the phosphorus to 8.6 mgm. per 100 cc. Normal rats on an ordinary diet failed to show this rise during irradiation. Burton[60] found in boys who had received some ultraviolet irradiation while on a diet high in calcium and phosphorus a high retention of these elements.

After daily exposures of gravid rats to sunlight, the lime of the fetuses increased 21.2

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[53] Orr, W. J., Holt, L. E., Jr., Wilkins, L., and Boone, F. H., *Am. J. Diseases of Children*, **26**, 362 (1923).

[54] Vignard, Mouriquand, Chassard, and Bernheim, *Lyon Medicale*, **132**, 1021 (1923); *Chem. Abs.*, **18**, 2382 (1924); Lesné, E., de Gennes, L., and Guillaumin, C., *Compt. rend.*, **177**, 291 (1923); *Chem. Abs.*, **17**, 3540 (1923); Howland, J., and Kramer, B., *Am. J. Diseases Children*, **22**, 105 (1921); *Chem. Abs.*, **17**, 413 (1923).

[55] Clark, J., *Am. J. Hyg*, **3**, 481 (1923); *Chem. Abs.*, **18**, 2366 (1924).

[56] Hart, E. B., H. Steenbock and C. A. Elvehjem, *J. Biol. Chem.*, **62**, 117 (1924).

[57] Orr, J. B., Henderson, J. M., and Magee, H. E., *Biochem. J.*, **19**, 569 (1925).

[58] Schultzer, P., *Compt. rend. soc. biol.*, **93**, 1005 (1925); *Chem. Abs.*, **20**, 1655 (1926); *Biochem. Z.*, **188**,, 409, 427 (1927); Mitchell, H. F., and Johnson, F., *Am. J. Physiol*, **72**, 143 (1925); Koch, E. M., and Cahan, M. H., *Am. J. Diseases of Children*, **34**, 187 (1927).

[59] Schultzer, P., *Compt. rend. soc. biol.*, **93**, 1008 (1925); *Chem. Abs.*, **20**, 1655 (1926).

[60] Burton, H. B., *J. Biol. Chem.*, **85**, 405 (1930).

per cent and the phosphate 19.2 per cent over that of the fetuses of non-irradiated rats. The phosphatase content, however, was not affected, according to Foa.[61]

Subsequent studies of the calcium and phosphorus in the blood serum in rickets have indicated that the disease may appear with either low phosphorus or low calcium or with both low in the serum. But if one is low and the other high there may be no rickets.[62] Kramer, Shear and Siegel[63] found the product of the calcium and phosphorus concentrations to be always thirty or less during rickets or during the cessation of calcification. When the product rises above forty, calcification may ensue no matter whether the healing is induced by cod-liver oil, phosphates, or artificially prepared vitamin D. There are, however, many recorded exceptions to this rule. Dietary ratios of calcium and phosphorus are important.[64] Many other papers deal with this topic, but are beyond the scope of this discussion.

At one time it was believed that an alteration of the pH of the substances in the intestinal tract was, in part at least, responsible for the failure of the proper absorption of calcium from the gut in rickets. Jephcott and Bacharach[65] stated that the alkalinity of the feces of animals on rachitic diets could be brought to the acid side of neutrality by irradiations or by administering cod-liver oil. It was assumed that determinations of the change in pH induced by various preparations containing vitamin D might be made the basis of an assay method for this vitamin. Wokes and Willimott[66] found that the method could not be applied to infants although they believed it gave satisfactory results in rats. Subsequent investigations, however, have shown the method unreliable.

The irradiation of nursing mothers whose breast milk had been failing was of general benefit in all of 53 cases in which the treatment was continued for some time, and was of aid in improving or retaining the milk supply in all but eleven of the cases.[67] Hess, Weinstock and Sherman[68] found that exposing a woman to the rays of a mercury-vapor quartz lamp every other day for a month produced antirachitic properties in her milk when fed to rats. During the control period the milk had no curative action. In similar experiments, Hirsch-Kauffmann and Wiener[69] found the quantity of the milk of irradiated mothers to be increased, although its chemical composition was unaltered except for a definite increase in vitamins C and D.

In children with various orthopedic disorders, exposure to all the sunshine available from May to August was not found to produce any symptoms characteristic of an overdose of vitamin D.[70]

APPLICATIONS IN ANIMAL HUSBANDRY

During the early development of irradiation therapy, attention was also devoted to the effects of ultraviolet light on farm animals. Hart, Steenbock and Jones[71] concluded that sunlight is a factor of economic importance in the production of pork in northern latitudes, and Maynard, Goldberg and Miller in New York[72] found that sunlight improves the assimilation of calcium from a deficient diet and prevents the development of leg weakness in pigs. In a general discussion, Price[73] stated that besides an adequate amount of calcium and phosphorus in the diet of pigs it is essential for their health and growth that there also must be present either the antirachitic vitamin or exposure to sunlight. Henderson[74] found that the calcium and phosphorus retention of pigs receiving a poorly balanced diet, with $P_2O_5:Ca:Mg$ as 3:1:1, was definitely increased by an irradiation of one hour per day for 24 days. No corresponding increase in body weight occurred, however.

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[61] Foa, P., *Boll. soc. ital. biol. sper.*, **11**, 845 (1936); *Chem. Abs.*, **31**, 2622 (1937).

[62] See Hess, A. F., "Rickets, Osteomalacia and Tetany," Philadelphia, Lea and Febinger, 1929. Note also Orr, W. J., Holt, L. E., Jr., Wilkins, L., and Boone, F. H., *Am. J. Diseases of Children*, **26**, 362 (1923); Hess, A. F., Weinstock, M., Rivkin, H., and Gross, J., *J. Biol. Chem.*, **87**, 37 (1930); Hess, A. F., Lewis, J. M., and Rivkin, H., *J. Am. Med. Assoc.*, **94**, 1885 (1930)

[63] Kramer, B., Shear, M. J., and Siegel, J., *J. Biol. Chem.*, **91**, 271, 723 (1931).

[64] See also Shohl, A. T., and Bennett, H. B., *J. Biol. Chem.*, **76**, 633 (1928); Reed, C. I., Struck, H. C., and Steck, I. E., "Vitamin D" Chicago, Univ. of Chicago Press, 1939.

[65] Jephcott, H., and Bacharach, A. L., *Biochem. J.*, **20**, 1351 (1926).

[66] Wokes, F., and Willimott, S. G., *Pharm. J.*, **118**, 752, 793 (1927).

[67] Chisholm, C., and McKillop, M., *Lancet*, **II**, 227 (1927); *Chem. Abs.*, **22**, 2384 (1928).

[68] Hess, A. F., Weinstock, M., and Sherman, E., *Proc. Soc. Exptl. Biol. Med.*, **23**, 636 (1926).

[69] Hirsch-Kauffmann, H., and Wiener, C., *Klin. Wochschr.*, **8**, 984 (1929); *Chem. Abs.*, **23**, 4970 (1929).

[70] Dodds, E. C., Robertson, J. D., and Roche, H. J., *Arch. Diseases of Childhood*, **9**, 91 (1934); *Chem. Abs.*, **28**, 4459 (1934).

[71] Hart, E. B., Steenbock, H., and Jones, J. H., *J. Biol. Chem.*, **61**, 775 (1924).

[72] Maynard, L. A., Goldberg, S. A., and Miller, R. C., *J. Biol. Chem.*, **65**, 643 (1925)

It was believed by Bohstedt, Insko and Fargo[75] that for the health of the suckling pig dependence must be placed upon the antirachitic properties of the feed of the sow rather than upon the use of ultraviolet light, helpful as this may be. According to Isaachsen,[76] irradiation of sows in the last six weeks of gestation and of sows with litters did not improve the growth or condition of the pigs. He believed that pigs are more likely to suffer from disordered mineral metabolism as a result of a deficiency of minerals in the food or from an incorrect calcium-to-phosphorus ratio than from a lack of fat-soluble vitamins. Sinclair[77] found exposure to either sunlight or artificial sources, as well as cod-liver oil feeding, to promote growth in the pig, the response being inversely proportional to the calcium content of the basal ration. The addition of calcium to the ration aided greatly in the prevention of leg stiffness, a condition resembling rickets. Irradiation increased the level of the blood calcium.

Calves also require vitamin D. Calves fed on rations deficient in it show declining growth rates at the twelfth to the fifteenth week; and after the twenty-fifth week little growth occurs.[78] A decline in the level of inorganic phosphorus in the blood serum precedes the onset of stiffness. The percentage of total ash in the dry, fat-free bones is reduced from the normal of 60 to 63 per cent to 45 to over 50 per cent in the rachitic bones. The breaking strength of the bones also is lowered. Ultraviolet irradiation, sunlight or the feeding of liberal amounts of sun-cured hay protects the calves from the vitamin D deficiency.

Bechdel, Landsburg and Hill[79] also noted the abnormal bone development, swollen joints, and slight paralysis of the rear quarters and bowed back of vitamin D-deficient calves. Although cod-liver oil promoted growth and thriftiness slightly better than did ultraviolet light treatment, the latter produced a slightly superior grade of bone. Direct sunlight is not required if the ration contains sufficient vitamin D.[80]

The vitamin D requirement of dogs has been studied by Morgan.[81] Symptoms of rickets have been developed in a newly weaned cat fed 24 days on the Steenbock diet deficient in calcium and vitamin D.[82]

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[73] Price, W. A., *Ind. Eng. Chem.*, **18**, 679 (1926).

[74] Henderson, J. M., *Biochem. J.*, **19**, 52 (1925); *Scottish J. Agr.*, **9**, 33 (1926); *Chem. Abs.*, **20**, 2523 (1926). See also Orr, J. B., Henderson, J. M., and Crichton, J. A., *Trans. Highland Agr. Soc. Scotland*, **38**, 88 (1926).

[75] Bohstedt, G., Insko, W. M., Jr., and Fargo, J. M., *Proc. Am. Soc. Animal Production*, 89 (1929), *Chem. Abs.*, **25**, 3695 (1931); see also Thalman, R. R., and Loeffel, W. J., *Proc. Am. Soc. Animal Production*, 83 (1928); *Chem. Abs.*, **25**, 3695 (1931).

[76] Isaachsen, H., *J. Agr. Sci.*, **22**, 460 (1932); *Chem. Abs.*, **27**, 1916 (1933).

[77] Sinclair, R. D., *Sci. Agr.*, **13**, 489 (1933); *Chem. Abs.*, **27**, 5787 (1933); Horn, V., *Biedermann's Zentralbl.* **B**, *Tierernahr.*, **6**, 203, 208 (1934); *Chem. Abs.*, **28**, 5855 (1934).

[78] Rupel, I. W., Bohstedt, G., and Hart, E. B., *Wisconsin Agr. Exp. Sta. Research Bull*, **115**, 40 pp. (1933); *Chem. Abs.*, **28**, 507 (1934).

[79] Bechdel, S. I., Landsburg, K. G., and Hill, O. J., *Pennsylvania Agr. Exp. Sta. Tech. Bull.*, **291**, 2 (1933); *Chem. Abs*, **28**, 3028 (1934).

[80] Olson, T. M., *S. Dakota Agr. Exp. Sta., Bull.* **319**, 2 (1938); *Chem Abs.*, **32**, 7970 (1938).

[81] Morgan, A. F., *North American Veterinarian*, **15**, No. 8, 24 (1934); *Chem. Abs.*, **29**, 201 (1935).

[82] Moody, C. A., *J. Home Econ.*, **28**, 696 (1936); *Chem. Abs.*, **31**, 436 (1937).

Irradiation and Poultry Culture. Because of the modern intensive methods of poultry culture, vitamin D deficiencies are quite common. Their remedy is a matter of considerable economic importance. Murray, Little and Bovie[83] found chicks exposed for only a few minutes each day to the rays of the mercury arc showed a more rapid formation of bone than did chicks exposed for many hours daily to direct sunlight.

Hughes, Titus and Moore[84] found that chicks fed on eggs from hens which were receiving direct sunlight developed normally, as shown by their general appearance and by the analysis of their blood and bones. Those fed on eggs from hens which received sunlight filtered through glass and supplemented by thirty minutes per day from a mercury arc developed some rickets. They were, however, in a better condition than those receiving eggs from hens which received no ultraviolet light other than that which came through a glass window. They believed thirty minutes of ultraviolet irradiation daily insufficient to enable hens to store sufficient antirachitic vitamin in their eggs to prevent entirely the development of rickets in chickens fed rations containing these eggs. Eggs of low antirachitic vitamin content do not have as high a hatchability as those with high vitamin content.[85]

Goodale[86] demonstrated that the amount of exposure to sunlight or ultraviolet light necessary for normal growth is but very small in the chick. Irradiations of one and ten minutes twice weekly at three feet from a mercury-vapor arc gave normal growth.[87]

DeVaney, Munsell and Titus[88] found that daily fifteen-minute irradiations with a carbon arc had approximately the same effect on vitamin D storage by hens as the addition of 1 per cent of cod-liver oil to the diet.

Hou[89] found rachitic chicks with intact preen glands to be cured when either the body, feet or head was irradiated. The degree of healing was greatest with the irradiation of the feet and least with the head. Rachitic chicks with the preen glands removed were not cured when the head was irradiated, but irradiation of the feet produced good healing. The substance which is activated when the feet are irradiated is apparently neither the preen gland material nor the circulating blood. Russell and Howard[90] delayed the onset of leg weakness in young chicks for about a week by an exposure to one day of winter sunlight through an ultraviolet transmitting material. There was also an indication of an effect on bone formation. A three-day exposure delayed the appearance of leg weakness about two and a half to three weeks and had a more enduring effect on bone formation.

Either cod-liver oil or ultraviolet irradiation of laying hens kept without access to direct sunlight or green feed increased the egg production, the thickness of the egg shells and the general condition of the birds, according to Hendricks, Lee and Godfrey.[91] Each of these methods of supplementing the vitamin D also tended to increase the egg weight and the hatchability of the eggs. Cod-liver oil was superior to fifteen minutes of daily irradiation under the conditions employed. Dove[92] believed the chick superior to the rat for vitamin D research because it is more sensitive than the latter to a deficiency of that vitamin. Payne and Hughes[93] found direct sunshine somewhat more effective than ultraviolet irradiations from artificial sources in increasing the calcium content of the hen blood, of eggs and of newly hatched chicks. Maughan and Maughan[94] noted that ultraviolet irradiation of hens increases the vitamin D content of the egg yolk.[95]

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[83] Murray, J. M., Little, C. C., and Bovie, W. T., *Maine Agr. Exp. Sta. Bull.* **320**, 141 (1924); *Chem. Abs.*, **19**, 3105 (1925).

[84] Hughes, J. S., Titus, R. W., and Moore, J. M., *Science*, **62**, 492 (1925); *Chem. Abs.*, **20**, 936 (1926); Hughes, J. S., Payne, L. F., Titus, R. W., and Moore, J. M., *J. Biol. Chem.*, **66**, 595 (1925).

[85] For the amounts of the vitamin required for the production of hatchable eggs, see Bethke, R. M., and Kennard, D. C., *Proc. Fourth World's Poultry Congress*, 342 (1930); *Chem. Abs.*, **25**, 4027 (1931). It has been suggested that sunlight may increase the hatchability of eggs by some mechanism other than vitamin D. Byerly, T. C., Titus, H. W., Ellis, N. R., and Nestler, R. B., *Poultry Sci.*, **16**, 322 (1937); *Chem. Abs.*, **31**, 8625 (1937).

[86] Goodale, H. D., *Am. J. Physiol.*, **79**, 44 (1926).

[87] Cf. also Price, W. A., *Science*, **63**, 1636 (1926); Russell, W. C., Massengale, O. N., and Howard, C. H., *J. Biol. Chem.*, **80**, 155 (1928); Maughan, G. H., and Dye, J. A., *J. Opt. Soc. Am.*, **20**, 279 (1930); *Proc. Soc. Exptl. Biol. Med.*, **28**, 106 (1930).

[88] De Vaney, G. M., Munsell, H. E., and Titus, H. W., *Poultry Sci.*, **12**, 215 (1933); *Chem. Abs.*, **27**, 5380 (1933).

[89] Hou, H.-C., *Chinese J. Physiol.*, **5**, 11 (1931); *Chem. Abs.*, **25**, 3037 (1931); see also Murphy, E. F., *J. Agr. Research*, **53**, 67 (1936); *Chem. Abs.*, **30**, 8319 (1936).

[90] Russell, W. C., and Howard, C. H., *J. Biol. Chem.*, **91**, 493 (1931).

Further studies on the vitamin D requirement of the chick have played an important part in the development of our knowledge of the chemistry of vitamin D and will be considered in the following chapter after the chemical changes underlying the formation of this substance have been discussed.

THE IRRADIATION OF FOODSTUFFS

During the years 1924 and 1925 it was discovered that, on analogy with the formation of antirachitic substances in the skin of irradiated animals, antirachitic potency is imparted to foodstuffs when these are submitted to the action of ultraviolet rays. Hume and Smith[96] were very near this important discovery when they reported that rats fed on a diet deficient in fat-soluble vitamins and kept in glass jars which had been exposed to quartz lamps for ten minutes every second day showed a prolongation of growth at a normal rate longer than that of controls kept in jars not so irradiated. Their work was conducted to determine whether the irradiation of the air played a part in the mechanism of the antirachitic resistance of irradiated animals. They showed definitely that ozone was not the effective agent, but overlooked the real cause of the beneficial effect they observed. Webster and Hill[97] showed that irradiated air could not have produced the beneficial results, and Hume and Smith later reported[98] that their results could be obtained only when the glass jars which were irradiated contained sawdust. When this was replaced by a piece of pine board, partial growth only resulted.[99] They had, however, missed their opportunity, for in the meantime Hess and Weinstock, as well as Steenbock and Black, had independently shown that certain foodstuffs can be rendered antirachitically active by irradiation.

On June 7, 1924, Hess reported the results of experiments conducted with Weinstock to the American Pediatrics Society[100] which indicated that vegetable oils can be endowed with antirachitic properties on irradiation. Like Smith and Hume, they had started by attempting to activate air by ultraviolet light but obtained completely negative results. Their first favorable results were obtained when they irradiated cottonseed oil.[101]

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[91] Hendricks, W. A., Lee, A. R., Godfrey, A. B., *J. Agr. Research*, **43**, 517 (1931); *Chem. Abs.*, **26**, 1324 (1932).

[92] Dove, W. F., *Maine Agr. Exp. Sta. Bull*, **360**, 172 (1931); *Chem Abs*, **27**, 1918 (1933).

[93] Payne, L. F., and Hughes, J. S, *Kansas Agr. Sta. Tech. Bull.*, **34**, 5 (1933); *Chem. Abs.*, **27**, 4277 (1933).

[94] Maughan, G. H., and Maughan, E., *Brit. J. Phys. Med.*, **7**, 137 (1932); *Chem. Abs.*, **27**, 5377 (1933).

[95] For calcium and phosphorus determinations in chicken blood, see Elvehjem, C. A. and Kline, B. E., *J. Biol. Chem.*, **103**, 733 (1933), and Higgins, G. M., Sheard, C., and Wilder, R. M., *Anat. Record*, **58**, 205 (1934).

[96] Hume, E. M, and Smith, H. H., *Biochem. J*, **17**, 364 (1923).

[97] Webster, T. A., and Hill, L., *Proc. Physiol. Soc.*, *J. Physiol*, **57**, LXXVIII (1923); *Chem. Abs.*, **18**, 278 (1924).

[98] Hume, E. M., and Smith, H. H., *Biochem. J.*, **18**, 1334 (1924).

[99] It was later shown by Rosenheim, O., and Webster, T. A., *Biochem. J.*, **20**, 1340 (1926) that a chloroform extract of irradiated sawdust has antirachitic activity.

[100] Hess, A. F., and Weinstock, M., *Abstracted in Am. J. Diseases of Children*, **28**, 256 (1924); **28**, 517 (1924). Also reported at a meeting of the New York Section, *American Chemical Society*, Jan. 9, 1925.

Steenbock and Black[102] in a paper received for publication April 18, 1924, described an experiment in which a ration of hog millet 84, purified casein, 12, and salt, was irradiated for ten minutes at a distance of 23 inches from a Cooper-Hewitt quartz mercury-vapor lamp with a three-fourths inch arc operated at 120 volts. When fed, this ration produced a pronounced stimulation of the growth of rats. They also succeeded in imparting growth-promoting and bone-calcifying properties to olive oil and lard by this method. The activation took place when the ration was irradiated in an open dish or in a stoppered Pyrex or quartz flask filled with air or carbon dioxide, but it did not occur when the ration was irradiated in a brown glass bottle. The ash content of the bones of the rats receiving the irradiated ration was increased in percentage over that of rats receiving the same ration before irradiation. It was found also that the irradiation of fats, otherwise inactive in curing rickets, caused them to become active. Rations which ordinarily produced a wide rachitic metaphysis in the shaft bones of rats became antirachitic and promptly effected a rapid and complete healing of the lesion. Hess, in his complete paper, showed that although cottonseed and linseed oils could be activated by irradiation, this was not possible in the case of mineral oil, and also that ozonized water and hydrogen peroxide afforded no protection to rats on a deficient diet. Steenbock and Daniels[103] successfully produced antirachitic properties in a wide variety of foods, which included wheat, rolled oats, corn, hominy, meats, milk, egg-yolk and the vegetable oils. They suggested that it is the sterols in the foods which are altered during the irradiation process. Spinach was rendered antirachitic by Chick and Roscoe[104] and cabbage by Mellanby and Killick.[105] That the irradiation of cod-liver oil did not increase its antirachitic potency was demonstrated by Daniels and Brooks[106] and by Wyman, Holmes, Smith, Stockbarger and Pigott.[107]

Hume, Smith and Smedley-Maclean[108] succeeded in inducing antirachitic activity in yeast fat by irradiation and Daniels and Pyle and Brooks[109] showed that the use of milk irradiated a half hour at a distance of two feet from a mercury arc rendered it capable of bringing about prompt improvement in young rats. Gates and Grant[110] found that in normal rabbits the feeding of cod-liver oil or irradiated products did not produce changes in the relative weights of endocrine organs such as the external parathyroid and the hypophysis, although these organs are hypertrophied in rabbits after repeated exposure to the quartz mercury arc. It was shown by Goldblatt and Moritz[111] that irradiation does not increase the quantity of vitamin A in fats but forms only the antirachitic D.

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[101] Hess, A. F., and Weinstock, M., *J. Biol. Chem.*, **62**, 301 (1924). Goldblatt, H., and Soames, K. M., *Biochem. J.*, **17**, 446 (1923), had found that the livers of irradiated animals restored the growth of animals which had been inhibited by feeding certain diets.

[102] Steenbock, H., and Black, A., *J. Biol. Chem.*, **61**, 408 (1924); see also *Science*, **60**, 224 (1924); *J. Biol. Chem.*, **62**, 209 (1924).

[103] Steenbock, H., and Daniels, A. L., *J. Am. Med Assoc.*, **84**, 1093 (1925).

[104] Chick, H., and Roscoe, M. H., *Biochem. J.*, **20**, 137 (1926).

[105] Mellanby, M., and Killick, E. M., *Proc. Physiol. Soc.*, **61**, xxiii (1926); *Chem Abs.*, **20**, 3488 (1926). See also Drummond, J. C., Rosenheim, O., and Coward, K. H., *J. Soc. Chem. Ind.*, **44**, 135T (1925). For a clinical investigation of the curative value of irradiated food, see Mackay, H. M. M., and Shaw, H. F., *Lancet*, **I**, 82 (1926).

[106] Daniels, A. L., and Brooks, L. M., *Proc. Soc. Exptl. Biol. Med.*, **24**, 971 (1927).

[107] Wyman, E. T., Holmes, A. D., Smith, L. W., Stockbarger, D. C, and Pigott, M. G., *Boston Med. & Surg. J.*, **195**, 525 (1926); *Am. J. Diseases Children*, **34**, 753 (1927). See also Haffner, F., and Pulewka, P., *Klin. Wochschr.*, **5**, 2113 (1926).

[108] Hume, E. M., Smith, H. H., and Smedley-Maclean, I., *Biochem. J.*, **22**, 27 (1928).

[109] Daniels, A. L., Pyle, S. I., and Brooks, L. M., *Proc. Soc. Exptl. Biol. Med.*, **23**, 821 (1926); *Chem. Abs.*, **21**, 1831 (1927).

[110] Gates, F. L., and Grant, J. H. B., *Proc. Soc. Exptl. Biol. Med.*, **24**, 59 (1926).

Among the earlier suggestions regarding the mechanism by which irradiation may function was one which has been repeatedly discussed, but is no longer considered significant. Kugelmass and McQuarrie suggested that irradiation so alters the substances of foods as to make them capable during subsequent slow oxidation of emitting ultraviolet rays which affect a photographic plate.[112] As they themselves subsequently pointed out, many substances exhibit the property of affecting a photographic plate, the Russell effect; it bears little or no relation to the production of antirachitic activity and it is unnecessary to consider here the large number of papers by other workers who sought to explain the effect of irradiation upon foodstuffs in terms of this phenomenon.

For some time it was believed that the origin of the vitamin in the livers of fish could be attributed to their ingestion of other smaller fish which had in turn ingested diatoms in which the vitamin had been produced photochemically. There is, however, considerable evidence against this. Leigh-Clare was unable to detect the vitamin in the marine diatom *Nitzschia closterium,* and others[113] were unable to demonstrate it in phyto- and zoö-plankton from the ocean.[114] Bills[115] found the capelin, the chief food of the Newfoundland cod, a poor source. The enormous differences in the potencies of the liver oils from various species of fish suggest species differences in the ability to synthesize the vitamin and not merely in its storage. Attempts to produce more vitamin D in fish livers by irradiation of the fish have been unsuccessful.

Sunflower oil can be activated by irradiation by sunlight or artificial ultraviolet light.[116] The same is true of peanut oil.[117] The irradiated mycelium of Aspergillus oryzae, added to the diet of chicks to the extent of 0.05 per cent, makes them superior in health, appetite and growth to the controls.[118] Sun-dried alfalfa contains small amounts of vitamin D.[119] Clover hay made with exposure to sunlight showed considerable calcifying power, but clover hay made in the dark was inactive. If excessively weathered, it is reduced in activity as compared with hay less exposed to dew and rain, but it may be improved by subsequent mercury-arc irradiation.[120]

The potency of sun-cured hays is, however, too feeble to prevent the development of rickets in growing chicks fed ether extracts of the hays equivalent to a high concentration of the hay in the ration.[121] From 7 to 10 gms. of dry corn silage per kg. of feed cures and prevents rickets in yearling calves and supplies sufficient vitamin D for normal growth and reproduction in dairy cows.[122]

Völtz and Kirsch believed that grass germinated in darkness contains some of the antirachitic vitamin.[123]

[111] Goldblatt, H., and Moritz, A A., *J. Biol. Chem* **71,** 127 (1926).

[112] Kugelmass, I. N., and McQuarrie, I., *Science,* **60,** 272 (1924); **62,** 87 (1925); Drummond, J. C., and Coward, K. H., *J. Soc. Chem. Ind.,* **44,** 255 (1925).

[113] Leigh-Clare, J. L., *Biochem. J.,* **21,** 368 (1927); Drummond, J C., and Gunther, E. R., *Nature,* **126,** 398 (1930).

[114] Belloc, G., Fabre, R., and Simonnet, H., *Compt. rend.,* **191,** 160 (1930).

[115] Bills, C. E., *J Biol. Chem.,* **72,** 751 (1927).

[116] Markar'yan, E. A., *Proc. Sci. Inst. Vitamin Research, U.S.S R,* **1,** 207 (1936); *Chem. Abs.,* **31,** 1854 (1937).

[117] Rondoni, P., *Sperimentale,* **80,** 443 (1926); *Chem. Abs.,* **21,** 761 (1927).

[118] Yokoyama, K., and Takata, R., *J. Agr. Chem. Soc. Japan,* **12,** 909 (1936); *Chem. Abs.,* **31,** 1468 (1937).

[119] Scheunert, A., and Schieblich, M., *Biedermann's Zentr. B. Tierernährung,* **6,** 112 (1934); *Chem. Abs.,* **28,** 5102 (1934).

[120] Steenbock, H., Hart, E B., Elvehjem, C. A., and Kletzien, S., *J. Biol. Chem.,* **66,** 425 (1925).

[121] See also Bechdel, S. I., Landsburg, K. G , and Hill, O J., *Pa. Agr. Exp. Sta. Tech. Bull* **291,** 2 (1933); *Chem. Abs.,* **28,** 2038 (1934).

[122] Bechtel, H. E., Huffman, C. F., Duncan, C. W., and Hoppert, C. A., *J. Dairy Sci.,* **19,** 359 (1936); *Chem. Abs.,* **30,** 5617 (1936).

[123] Völtz, W., and Kirsch, W., *Biochem. Z.,* **186,** 255 (1927).

Chapter 39

The Photochemistry of the Formation of Vitamin D

EARLY OBSERVATIONS REGARDING THE PRECURSOR

Following the discovery of the ability of irradiation to render foodstuffs antirachitically active, there began an active search to determine which components of these materials are effectively altered during the irradiation. Such components as chlorophyll, hemoglobin, glycerol, starch, alkaloids and the phosphatides of egg-yolk were soon eliminated.[1] It was soon demonstrated that the vitamin is a component of only the unsaponifiable fraction of irradiated oils and that the chief components of the unsaponifiable portions of the oils, the sterols, have the property of being activated by irradiation.[2] This was shown in the case of the phytosterol prepared from cottonseed oil and of cholesterol isolated from brain tissue. Since it was known that the skin of animals contains much cholesterol, Hess suggested that when the animal is irradiated it is the cholesterol of the skin which is changed, or as it was then said, activated.[2a]

Steenbock and Black[3] were able to impart antirachitic activity to purified cholesterol by irradiation with either a mercury arc, a carbon arc or direct sunlight. They observed the significant fact that irradiation for prolonged periods destroyed the activity of natural cod-liver oil and also the activity artificially produced by shorter irradiations of vegetable oils, although in darkness the activity was maintained as long as ten months. They believed that old oils which had become acid could no longer be activated, although this was not held due to the acidity as such, since the addition of oleic acid to the oil did not interfere with the process of activation.

That the antirachitic properties of irradiated cholesterol, like those of cod-liver oil, can be destroyed by heating with butyronitrile was believed by Bills[4] to support, although not to prove, the identity of the irradiation product of cholesterol with the vitamin of cod-liver oil. That the rays which render cholesterol active are those which cure the animal in irradiation therapy was shown by Hess and Weinstock.[5] They also showed that the dihydroderivatives of cholesterol or of the phytosterol of wheat could not be made to acquire antirachitic activity by irradiation. This indicated unsaturation to be a necessary, but not a sufficient condition, determining the ability of a compound to function as a precursor of the vitamin.

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[1] Hess, A. F., Weinstock, M., *J. Biol. Chem.*, **63**, 297 (1925); **62**, 301 (1924); Drummond, J. C., Coward, K. H., and Rosenheim, O., *J. Soc. Chem. Ind.*, **44**, 123T (1925). See also Dutcher, R. A., and Kruger, J. H., *J. Biol. Chem.*, **69**, 277 (1926). Waltner, K., *Magyar Orvosi Arch.*, **28**, 6, 13, 19 (1927); *Chem. Abs.* **21**, 1480 (1927), claimed to have "activated" tyrosine, but this was disproved by Kon, S. K., and Moore, T., *Biochem. J.*, **21**, 1368 (1927) and later by Waltner himself, *Magyar Orvosi Arch.*, **29**, 151 (1928); *Chem. Abs.*, **22**, 4155 (1928).

[2] Hess, A. F., Weinstock, M., and Hellman, F. D., *Proc. Soc. Exptl. Biol. Med.*, **22**, 76 (1924).

[2a] This term must not be confused with photochemical activation in the sense of excitation of a molecule to a higher energy level.

[3] Steenbock, H., and Black, A., *J. Biol. Chem.*, **64**, 263 (1925).

[4] Bills, C. E., *J. Biol. Chem.*, **66**, 451 (1925).

[5] Hess, A. F., and Weinstock, M., *J. Biol. Chem.*, **64**, 181 (1925).

Rosenheim[6] verified the activatability of cholesterol and, with Webster,[7] obtained a fraction of the irradiated material which protected against rickets when given in daily doses of but 0.01 mg.

Attempts were soon made to activate various derivatives of cholesterol and analogous compounds. Hottinger[8] found that the salts of the bile acids could not be rendered antirachitic by irradiation. Although he obtained no indications of growth-promoting power in irradiated solutions of cholesterol acetate or palmitate, Hottinger stated that cholesterol oleate can be made antirachitic and Bills and McDonald[9] found the same to be true of the acetate, isobutyrate and benzoate although not of cholesterol ethers. They established that the double bond of cholesterol must remain intact for the change to occur, although the alcohol group may be esterified. Schlutz, Ziegler and Morse[10] definitely eliminated the oxidation products of cholesterol as α- and β-cholesteryl oxides, hydroxycholesterol, and α-cholestantriol as either the vitamin or its precursor. They made the suggestion that the provitamin of cholesterol might have been, both in their own experiments and those of others, some difficultly removable impurity rather than cholesterol itself. Epicholesterol cannot be rendered antirachitic by irradiation.[11]

According to Hume and Smith,[12] the sterols obtained from the small Siak-illipe nut can be activated. Hess and Anderson[13] found that irradiation makes α-sitosterol strongly antirachitic, but does not affect the β- and γ-sitosterols.[14]

Von Euler, von Euler and Rydbom[15] found it possible to activate the sterols extracted from dried red blood cells.[16] They also observed the possibility of activating the phosphate and phosphite esters of sterols. Coprosterol, being an isomer of dihydrocholesterol and therefore lacking double bonds, cannot be activated.[17] The same is true of cerevisterol from yeast.[18]

Early Views as to the Change Involved. Certain features of the mechanism of the irradiation process were made clear even in this early phase of the investigations. No change in the elementary composition of cholesterol could be detected by Hess, Weinstock and Sherman[19] after an hour of irradiation. This was an essentially correct observation which did not receive sufficient credence, since it was thought that combustion methods might not detect a slight amount of change in the composition of the highly active, but unisolated product of the irradiation. Windaus,[20] however, made the suggestion that the activation might involve a stereoisomerization to *allo*-cholesterol, a suggestion which proved incorrect. The melting point of a sample of cholesterol which melted sharply at 146°C. was altered[21] by irradiation so that it melted over a range of about 20°C. Some of its color reactions, notably the Whitby test, became negative.

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[6] Rosenheim, O., *Lancet*, **I**, 1025 (1925); see also Kramer, B., Shear, M. J., and Shelling, D. H., *J. Biol. Chem.*, **71**, 213, 221 (1926)

[7] Rosenheim, O., and Webster, T. A., *Biochem. J.*, **20**, 537 (1926).

[8] Hottinger, A., *Z. Kinderheilk.*, **43**, 8 (1927); *Chem. Zentr.* **II**, 2036 (1928), *Chem. Abs*, **21**, 3219 (1927).

[9] Bills, C. E., and McDonald, F. G., *J. Biol. Chem.*, **72**, 13 (1927).

[10] Schlutz, F. W., Ziegler, M. R., and Morse, M., *J. Biol. Chem.*, **73**, 209 (1927).

[11] Marker, R E., Kamm, O., Oakwood, T. S., and Laucius, J. F., *J. Am. Chem. Soc.*, **58**, 1948 (1936).

[12] Hume, E. M., and Smith, H. H., *Biochem. J.*, **20**, 340 (1926).

[13] Hess, A. F., and Anderson, R. J., *J. Biol. Chem.*, **74**, 651 (1927).

[14] For the irradiation of anhydrous lanolin, see Bernhard, A., and Drekter, I. J., *J. Biol. Chem.*, **93**, 1 (1931); Töpelmann, H., and Schuknecht, W., *Z. Vitaminforschung*, **4**, 111 (1935); *Chem. Abs*, **29**, 5596 (1935); Schieblich, M., and Pallaske, G, *Deut. Med. Wochschr.*, **61**, 957 (1935) Zurukzoglu, S., and Mündel, O., *Z. Vitaminforschung*, **6**, 125 (1937); *Chem. Abs.*, **31**, 5446 (1937).

[15] von Euler, H., von Euler, B., and Rydbom, M., *Arch. Med. Skand.*, **68**, 371 (1928); *Chem. Abs.*, **22**, 4591 (1927).

[16] Even cholesterol or lipins from the snail can acquire antirachitic properties, Mouriquand, G., and Leulier, A., *Compt. rend.*, **188**, 1701 (1929).

[17] Rosenheim, O., and Webster, T. A., *Biochem. J.*, **20**, 537 (1926).

[18] Honeywell, E. M., and Bills, C. E., *J. Biol. Chem.*, **99**, 71 (1932).

[19] Hess, A. F., Weinstock, M., and Sherman, E., *J. Biol. Chem.*, **66**, 145 (1925).

[20] Windaus, A., and Hess, A, *Nachr. Ges. Wiss. Göttingen, Math. Phys. Kl.*, 175 (1926); *Chem. Abs.*, **22**, 256 (1928).

Oxygen was not essential to the conversion, since Hess, Weinstock and Sherman[22] showed that it could be effected by irradiation under nitrogen. Contradictory reports by Tiede and Reyher in the case of milk[23] may have been due to their reliance upon odor and taste rather than an actual test of potency. Hess, Weinstock and Sherman[24] believed an active fraction from irradiated cholesterol to be soluble in liquid ammonia. Attempts by these authors to fractionate the altered material from unchanged cholesterol by recrystallization methods with alcohol as solvent[25] were unsuccessful; a gradual loss of the antirachitic activity occurred. Nitzescu, Popoviciu[26] and Denes-Goetz claimed to have attained some degree of concentration by such methods.

A method which proved extremely fruitful was introduced by Nelson and Steenbock.[27] It consisted in the precipitation of the unaltered cholesterol as a molecular compound with digitonin, a much used method in sterol chemistry. The antirachitic factor was found not to be precipitated by this reagent. The method is employed quantitatively for determining the extent to which the cholesterol has been altered during a given irradiation. The difference between the amount of sterol treated and that which can be recovered by digitonin precipitation represents the amount which has been photochemically altered. Cholesterol liberated from the digitonin precipitate was found to be capable of activation on renewed irradiation. Similar results were obtained by Hess, Weinstock and Sherman.[28]

On prolonged irradiation the antirachitic activity first produced is destroyed. This process is irreversible.[29] Prolonged irradiation of cod-liver oil deprives it of its antirachitic vitamin. This, Adam[30] suggested, might be due to an oxidative cleavage with the production of an acid, the iodine number being inversely proportional to the time of irradiation. Hottinger[31] also observed that the antirachitic material is irreversibly destroyed by heating it at 150 to 200°C. and partially so at 100 to 120°C. Bills and Brickwedde[32] found that greater activity could be attained by irradiating cholesterol at liquid air temperature than at room temperature. Cholesterol solutions in oils irradiated in oxygen exhibit a change in dielectric constant, according to Ellinger.[33] This is attributed to an oxidation process rather than to the formation of the antirachitic substance since it does not occur during irradiations in the absence of air, under which conditions the vitamin can be formed. Bills and McDonald[34] succeeded in obtaining a slight degree of activation of cholesterol without irradiation by treatment with a certain fuller's earth called floridin.

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[21] Von Euler, H., Myrbäck, K., and Karlsson, S., *Z physiol Chem*, **157,** 263 (1926).

[22] Hess, A. F., Weinstock, M., and Sherman, E., *J. Biol. Chem.*, **66,** 145 (1925).

[23] Tiede, E., and Reyher, P., *Naturwiss.*, **14,** 741 (1926).

[24] Hess, A. F., Weinstock, M., and Sherman, E., *J. Biol. Chem.*, **70,** 123 (1926).

[25] Hess, A. F., Weinstock, M., and Sherman, E, *J. Biol Chem.*, **66,** 145 (1925).

[26] Nitzescu, I. I., Popoviciu, G., and Denes-Goetz, J., *Bull. soc. chim. biol.*, **9,** 126 (1927); *Brit. Chem. Abs.*, **1927A,** 487.

[27] Nelson, E. M., and Steenbock, H., *J. Biol. Chem.*, **64,** 299 (1925).

[28] Hess, A. F., Weinstock, M., and Sherman, E., *J. Biol. Chem*, **70,** 123 (1926). See also Nitzescu, I. I, Popoviciu, G., and Denes-Goetz, J., *Bull. soc. chim. biol.*, **9,** 126 (1927); *Chem Abs.*, **21,** 487 (1927). Occasional inaccurate statements imply that the vitamin may be precipitated by digitonin, *e.g.*, Beumer, H., *Klin. Wochschr.*, **5,** 1952 (1926). Thus Hess, A. F., and Sherman, E., *Proc. Soc Exptl. Biol. Med.*, **23,** 169 (1925) believed irradiated cholesterol to delay the hemolytic action of digitonin by binding it more readily than does cholesterol. See also Hottinger, A., *Z. Kinderheilk*, **43,** 8 (1927); *Chem. Zentr.* **II,** 2036 (1928); *Chem. Abs.*, **21,** 3219 (1927).

[29] Hess, A. F., Weinstock, M., and Sherman, E., *J. Biol. Chem.*, **66,** 145 (1925).

[30] Adam, A., *Klin. Wochschr.*, **5,** 1648 (1926); *Chem. Abs.*, **21,** 119 (1927).

[31] Hottinger, A., *Z. Kinderheilk.*, **43,** 8 (1927); *Chem. Zentr.* **II,** 2036 (1928); *Chem. Abs.*, **21,** 3219 (1927).

[32] Bills, C. E., and Brickwedde, F. G., *Nature*, **121,** 452 (1928).

ULTRAVIOLET ABSORPTION STUDIES AND ERGOSTEROL AS A PROVITAMIN

Studies of the alterations of the absorption spectra of sterols during the formation of vitamin D directed attention to ergosterol, a difficultly removable contaminant of cholesterol as the precursor.[35] Von Euler[36] had found that the ability of various oils to be converted into the vitamin did not parallel their cholesterol content. It has subsequently been demonstrated that the important contaminant of cholesterol is not predominantly ergosterol, but rather the spectroscopically indistinguishable 7-dehydrocholesterol.

It was first shown by Hess and Weinstock[37] that although the spectrum of dihydrocholesterol, which cannot be activated, remained unaltered during its irradiation, that of cholesterol underwent a series of changes. Irradiation for about an hour decreased the absorption by the cholesterol, but prolonged irradiation had the opposite effect. After 17 hours, the material had become somewhat yellow in color and melted at a lower temperature, and after 30 hours it was opaque to both the ultraviolet and blue rays. Schlutz and Morse[38] made the premature suggestion that the early disappearance of the absorption bands of cholesterol might be taken as an index of the potency attained, thus avoiding the necessity of prolonged animal experiments. Subsequent developments, however, showed the spectrographic changes to be extremely complicated.

Soon, however, other workers in three laboratories showed that some of the absorption bands exhibited by cholesterol were really due to an impurity. Rosenheim and Webster[39] showed that when the cholesterol had been purified through the dibromide it could no longer be made antirachitic by irradiation. The usual methods of purification, however, did not remove the impurity which is capable of producing the vitamin on irradiation. This is an instance of a peculiar difficulty inherent in the chemistry of the sterols in general. These substances have a tendency to form loose associations with each other, with their derivatives, and with other compounds, notably the bile acids, which renders it very difficult to obtain pure compounds by even many recrystallizations. Heilbron, Morton and Kamm[40] by fractional crystallization of cholesterol from ethyl acetate, concentrated a substance in the least soluble fraction which had three well-defined absorption bands at 2930, 2800 and 2690A. These disappeared when the substance was irradiated, either in the solid state or in solution in alcohol or ether. At Göttingen, Pohl[41] found a sample of cholesterol which exhibited an inflection at about 2700A, a peak at about 2800 and an inflection at about 2900A to be altered by irradiation by a magnesium spark in such a way as to increase the transmission between 2500 and 3100A. As great a change could be produced in ten minutes with a magnesium spark with strong lines between 2800 and 2850A as could be obtained with the unfiltered mercury arc in an hour. By subtraction of the absorption curve obtained after an irradiation of twenty minutes from the original absorption curve of the sample there was obtained an absorption curve of the material which had been altered by the irradiation. This curve was subsequently shown to correspond to the absorption curve of ergosterol.[42] The decrease in extinction values at 2800A, indicated that, had the original absorption band truly belonged to cholesterol, about half of the sample must have been altered during the irradiation. Actually, however, at least 99.5 per cent of the original cholesterol could be recovered unchanged after such a treatment. The absorption which is altered during the irradiation must, therefore, be that of a contaminant. From the extinction values of ergosterol, Pohl concluded that his original cholesterol samples had been contaminated with this sterol to the extent of about one in 6000. Bills, Honeywell and McNair[43] found the ergosterol bands shown by samples of cholesterol could be made to disappear by treatment with charcoal. The original samples had been contaminated to the extent of about 1.2 parts per thousand. The disappearance of the ergosterol bands of ordinary cholesterol and bromide-purified cholesterol to which ergosterol had been added, during treatment with a permanganate solution was so similar as to afford further evidence that ergosterol is at least a contaminant of cholesterol. Rosenheim and Webster[44] estimated the intensity of the absorption by ergosterol to be from 1500 to 2000 times that of brain cholesterol. By irradiating ergosterol itself rather than cholesterol they soon obtained far more potent preparations than those obtainable by the irradiation of cholesterol. Similar results have been reported for the case of the zymosterol of yeast.[45]

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[33] Ellinger, P., *Arch. exptl. Path. Pharmakol.*, **122**, 238 (1927); see also Remezov, I., *Biochem. Z.*, **248**, 256 (1932); **250**, 560 (1932); Yeremenkow, N. P., *Arch. sci. biol. (U.S.S.R.)*, 37, 509, 542 (1935); *Chem. Abs.*, **30**, 6021, 7041 (1936).

[34] Bills, C. E., and McDonald, F. G., *J. Biol. Chem.*, **68**, 821 (1926); **72**, 1 (1927); see also Yoder, L., *Science*, **80**, 385 (1934).

[35] This work has been reviewed by Loofbourow, J. R , *Bull. Basic. Sci. Research*, **3**, 101, 201 (1931); **4**, 59 (1932).

[36] von Euler, H., *Arch. Kemi Mineral Geol.*, **9**, 28 (1925).

[37] Hess, A. F., and Weinstock, M., *J. Biol. Chem.*, **64**, 181, 193 (1925); Hess, A. F., Weinstock, M., and Helman, F. D., *Proc. Soc. Exptl. Biol. Med.*, **22**, 227 (1924-5).

[38] Schlutz, F. W., and Morse, M., *Am. J. Diseases of Children*, **30**, 199 (1925); Schlutz, F. W., and Ziegler, M. R., *J. Biol. Chem.*, **69**, 415 (1926)

[39] Rosenheim, O., and Webster, T. A., *J. Soc. Chem. Ind.*, **45**, 932 (1926); *Biochem. J.*, **20**, 537 (1926).

[40] Heilbron, I., Morton, R. A., and Kamm, E. D., *J. Soc. Chem. Ind.*, **45**, 932 (1926); *Biochem. J.*, **21**, 78 (1927).

Ergosterol is a sterol first isolated by Tanret from ergot, a fungus on rye, a material which itself is said to have a definite antirachitic action on dogs.[46] It is also present in yeast, and is apparently present in both animal and plant cells as a contaminant of their respective sterols. Its occurrence in such vegetable oils as that of the peanut has been reported by Morton, Heilbron and Kamm[47] and it was detected in animal skin (pig) by Rosenheim and Webster.[48] The structures of cholesterol and ergosterol are given below. There remains one doubtful point in the latter. The formula given is that of Windaus, in which one double bond is placed in the C_7—C_8 position. Heilbron places it in the C_8—C_9 position. This would mean that the two double bonds in Ring B are not in conjugation. Against this Dimroth and Trautmann[49] point out that such a structure would not be expected to give the characteristic absorption bands of ergosterol. They also show that ergostatriene, the unsaturated parent hydrocarbon of ergosterol, and 7-dehydrocholestene each have the same absorption spectrum as ergosterol, so that the hydroxyl group at position 3 does not influence the absorption.[50]

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[41] Pohl, R., *Nachr. Ges. Wiss. Göttingen, Math. Physik. Kl.*, 142 (1926).

[42] Pohl, R., *Naturwiss.*, **15**, 433 (1927); *Nachr. Ges. Wiss. Göttingen, Math. Physik. Kl.*, 185 (1927).

[43] Bills, C. E., Honeywell, E. M., and McNair, W. A., *J. Biol. Chem.*, **76**, 251 (1928); Bills, C. E., *Ibid.*, **66**, 451 (1925).

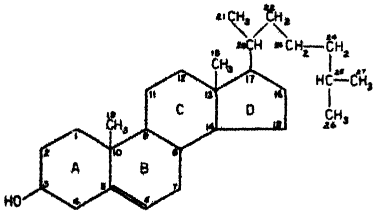
[44] Rosenheim, O., and Webster, T. A., *Lancet*, **I**, 306 (1927); *Biochem. J.*, **21**, 381 (1927).

[45] Fabre, R., and Simonnet, H., *Compt. rend.*, **188**, 1312 (1929); Hume, E. M., Smith, H. H., and Smedley-MacLean, I., *J. Soc. Chem. Ind.*, **47**, 537 (1928); Hess, A. F., and Anderson, R. J., *J. Biol. Chem.*, **74**, 652 (1927).

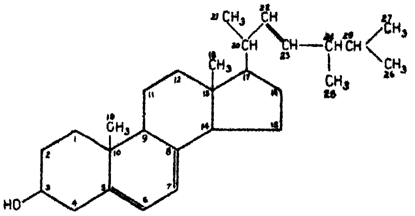
[46] Mellanby, E., Surie, E., and Harrison, D. C., *Proc. Physiol. Soc., J. Physiol*, **65**, xxix (1928); *Chem. Abs.*, **23**, 1163 (1929); *Biochem. J.*, **23**, 710 (1929).

[47] Morton, R. A., Heilbron, I., and Kamm, E., *Biochem. J.*, **21**, 1279 (1927).

[48] Rosenheim, O., and Webster, T. A., *Biochem. J.*, **21**, 389 (1927).



Cholesterol



Ergosterol

Various related compounds have been irradiated, with negative results.[51] Among these were Reindel's isoergosterol[52] and the fungisterol of ergot.[53] Positive results claimed by Windaus in the case of digitaligenin,[54] which like ergosterol contains three double bonds, could not be confirmed by Rosenheim and Webster. The absorption spectrum of ergosterol is given in Figure 152. During the irradiation of ergosterol, some of its color reactions suffer alteration. In the Meesemaecker reaction,[55] the addition of acetic anhydride and anhydrous zinc chloride to a chloroform solution of ergosterol produces a rose color which changes to a stable green. After irradiation of the ergosterol solution, however, only the green color results.[56]

INFORMATION YIELDED BY STUDIES OF THE CHANGES IN ULTRAVIOLET ABSORPTION OF ERGOSTEROL DURING IRRADIATION.

Many of the earlier papers dealing with the conversion of ergosterol into an antirachitic product relied chiefly upon the evidence yielded by the changes in absorption for conclusions as to the nature of the processes occurring. The first object was to obtain from such studies a clear indication of the absorption spectrum of the antirachitic substance. The results were extremely confusing and led various workers successively to consider three different absorption maxima as characterizing the vitamin. It was at first believed to have a prominent band at about 2450A, but this was subsequently shown to characterize instead overirradiated solutions of but little antirachitic activity. Then it was thought that a band near 2800A, with greater extinction coefficients than that of ergosterol, might represent the vitamin; but this was later found in error due to the fact, since demonstrated in the laboratory of Windaus, that a number of reactions are involved in the formation of the vitamin, each attended by absorption changes and in part occurring simultaneously. Finally, it has been established that the antirachitic material has an absorption band in the region of 2650A.

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[49] Dimroth, K., and Trautmann, G., *Ber.*, **69B**, 669 (1936).

[50] See, however, Heilbron, I. M., *J. Soc Chem. Ind.*, **55**, 129 (1936).

[51] Rosenheim, O., and Webster, T. A., *Biochem. J.*, **22**, 762 (1928).

[52] Reindel, F., Walter, E., and Rauch, H, *Annalen*, **452**, 34 (1927).

[53] Rosenheim, O., and Webster, T. A., *Lancet*, **II**, 622 (1927).

[54] Windaus, A., *Z. angew. Chem.*, **40**, 697 (1927); Windaus, A., and Holtz, F., *Nachr. Ges. Wiss. Göttingen, Math. Physik. Kl.*, 217 (1927); *Chem. Abs.*, **22**, 3910 (1928).

[55] Meesemaecker, R., *Compt. Rend.*, **190**, 216 (1930); *Brit. Chem. Abs.*, **A**, 477 (1930).

[56] See also Häussler, E. P., and Brauchli, E., *Helv. Chim. Acta.*, **12**, 187 (1929) for the effects of irradiation on the Tortelli and Jaffe reaction.

Pohl[57] found that irradiation of ergosterol solutions with a magnesium spark for 25 minutes caused a fading of the 2800A band of ergosterol resulting in a change in the absorption spectrum. By subtracting the original curve from that after irradiation, Pohl was led to conclude that the true absorption spectrum of the vitamin would be characterized by a band with a maximum at 2450A. Similar conclusions were reached independently by Morton, Heilbron and Kamm,[58] who observed that the band at 2470A disappeared on prolonged irradiation, just as vitamin D was known to be destroyed. Their assays, carried out by the fecal alkalinity method, were not sufficiently accurate to demonstrate that overirradiation had already occurred when the 2470A band appeared. Confirmation of the general course of the spectographic changes was afforded by Van Stolk, Dureuil and Heudebert.[59]

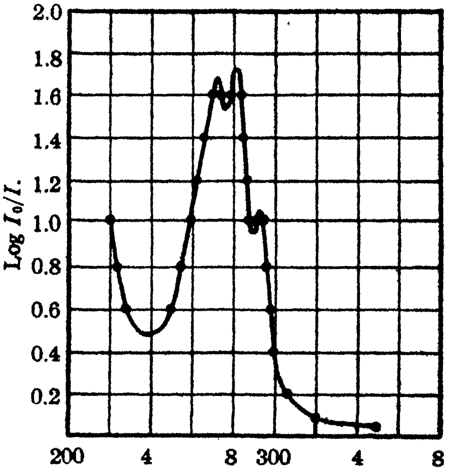

FIGURE 152.

Absorption of Ergosterol (Marshall and Knudson, *Journal American Chemical Society*).

The erroneous correlation of the band near 2470A with that of the vitamin led to the use of the appearance of this band as a criterion of suitable time and conditions of irradiation in commercial preparations of irradiated ergosterol introduced in Europe, and which were therefore actually overirradiated so that they contained toxic products. (See Chapter 38).

Bills, Honeywell and Cox[60] presented a curve for the potency of a 1 gm. per liter alcoholic solution of ergosterol after various times of irradiation in 2 cm. quartz cells directly in contact with the window of a water-cooled Kromayer lamp. Comparison of this curve with the absorption spectra obtained after various times of irradiation showed that the maximum potency had been attained and passed before the band near 2450A had become prominent, and that by the time it had reached its maximum, the potency had been largely destroyed. In a repetition of the work during which air was admitted into the cell, this band developed and faded more rapidly, but the activation curve was essentially the same as before. They believed that although oxidation might play a part in the destruction of the 2480A band, it was probably not concerned in the formation of the vitamin. They stated that the band at 2480 occurs also in the spectrum of an isoergosterol of Reindl, Walter and Rauch.[61] Rosenheim and Webster also made it clear[62] that the 2450A band is characteristic of a degradation product and not of the vitamin. Tixier[63] concluded that the time when the absorption at 2537A is a maximum does not correspond to the time at which the antirachitic potency is greatest.

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[57] Pohl, R., *Naturwiss.*, **15**, 433 (1927)

[58] Morton, R. A., Heilbron, I. M., and Kamm, E. D., *J. Chem. Soc.*, 2000 (1927); see also Rosenheim, O., and Webster, T. A., *Lancet*, **II**, 622 (1927).

[59] Van Stolk, D., Dureuil, E., and Heudebert, *Compt. rend.*, **187**, 854 (1928); *Chem. Abs.*, **23**, 1166 (1929).

[60] Bills, C. E., Honeywell, E. M., and Cox, W. M., Jr., *J. Biol. Chem.*, **80**, 557 (1928).

Smakula[64] continued the work of Pohl but used only very short irradiation periods[65] and excluded oxygen which he thought might alter some of the irradiation products. His observations eliminated the 2470A band as the vitamin absorption. He suggested that the true vitamin bands might be located near 2600 and 2900A.

Webster and Bourdillon[66] believed, as did Smakula, that during the early periods of irradiation, the absorption increases in a manner suggestive of the possibility that the vitamin has a band near 2800A. However, after the removal of unaltered ergosterol by digitonin precipitation, the absorption curve of the remaining solution showed less absorption than did that of ergosterol except in the region of wave-lengths longer than 3000A. This apparent decrease in absorption in the regions 2800 to 2900 they attributed to the simultaneous formation of some product without either absorption or antirachitic activity. Their belief that the vitamin absorbed at 2800A was founded in part upon the fact that a reirradiation of active preparations by filtered rays free from wave-lengths shorter than 2600A destroyed their antirachitic activity.

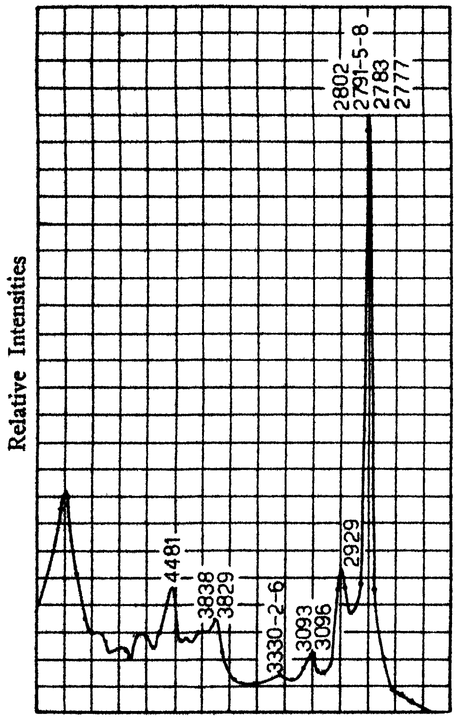

FIGURE 153.

Energy Distribution of Magnesium Spark (From Marshall and Knudson, *Journal of the American Chemical Society*).

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[61] For further discussion of early work on the significance of this band, see Morrison, R. R., and Clark, L. H., *Brit. J. Radiology*, **2**, 307 (1929); *Chem. Abs.*, **23**, 5221 (1929); Fabre, R., and Simonnet, H., *Bull. soc. chim. biol.*, **10**, 1100 (1928); *Chem. Abs.*, **23**, 421 (1929); *Compt. rend. soc. biol.*, **99**, 193 (1928); *Chem. Abs.*, **22**, 3438 (1928); *Compt. rend.*, **188**, 424 (1929); *J. Pharm. chim.*, **9–10**, 331 (1929); Delaplace, R., and Rebière, G., *Compt. rend.*, **188**, 1169 (1929); Castille, A., and Ruppol, E., *Bull. Acad. Roy. Med. Belg.*, 799 (1929).

[62] Rosenheim, O., and Webster, T., *Biochem. J.*, **22**, 1223 (1928).

[63] Tixier, G., *Compt. rend.*, **188**, 206 (1929).

[64] Smakula, A., *Nachr. Ges. Wiss. Göttingen, Math. Physik. Kl.*, 49 (1928); *Chem Abs.*, **23**, 1157 (1929).

[65] See also Knudson, A., and Moore, C. N., *J. Biol. Chem.*, **81**, 49 (1929).

[66] Webster, T. A., and Bourdillon, R. B., *J. Soc. Chem. Ind.*, **47**, 1060 (1928); *Biochem. J.*, **22**, 1223 (1928).

The importance of a band at 2650A was first emphasized by Reerink and van Wijk.[67] These workers studied separately the effects of irradiation by wave-lengths longer than about 2750A and by shorter wave-lengths. Their long wave-lengths were obtained by the use of either a mercury arc or a magnesium spark (Fig. 153), in either case filtered through a half cm. of a 10-per cent benzene solution. Hexane solutions of ergosterol were irradiated in quartz containers completely filled which had been cooled in solid carbon dioxide and evacuated by a high-vacuum pump, before sealing off. During the first fifteen minutes of irradiation there was an increased absorption throughout a large portion of the spectrum, later followed by a lessening of the absorption in the long wave-length region with but little change in the shorter wave-length region. The maximum at 2820A diminished from the beginning but that at 2715A increased at first. The nature of the changes in the absorption curves suggested that several substances were formed successively. By the use of very short irradiation periods they found an early formed product to have the absorption curve obtained by the difference method of Pohl and Smakula indicated in Fig. 154. This was called product *L*. This absorption could be confirmed as that of the residue after removal of the unchanged ergosterol by digitonin precipitation if special precautions were taken to exclude oxygen. The single broad absorption band with its maximum near 2650A was attributed to the vitamin. There were some indications that it could be obtained as crystals at low temperatures. These authors believed that for irradiation periods up to about fifteen minutes, when 50 per cent of the ergosterol had been altered, practically all of the product consisted of the vitamin. After longer irradiation periods, 45 minutes to forty hours, larger quantities of secondary products with less absorption near 2700A appeared. After 25 hours of irradiation the ergosterol bands at 2800 and 2900A had practically disappeared and a broad band between 2400 and 2500A became prominent. Animal experiments by Everse

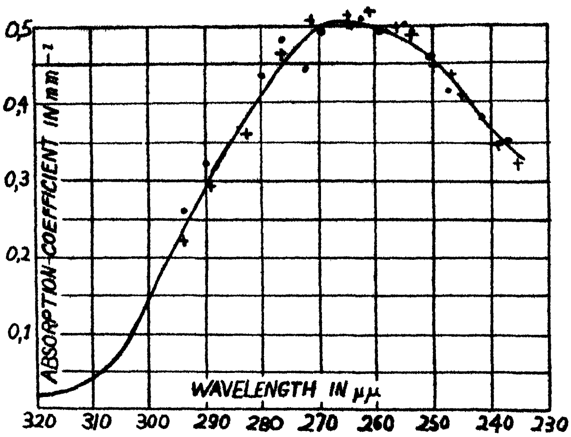

FIGURE 154. Absorption of Product L of Reerink and van Wijk *(Biochemical Journal)*.

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[67] Reerink, E. H., and van Wijk, A., *Biochem. J.*, 23, 1294 (1929); *Proc. Acad. Sci. Amsterdam*, 32, 845 (1929); *Chem. Abs.*, 24, 1408 (1930); *Nederland. Maandschr. Geneesk.*, 17, 1 (1930); *Chem. Abs.*, 24, 4534 (1930); *Nature*, 122, 648 (1928).

and van Niekerk[68] indicated the antirachitic activity to be closely correlated with the amount of this substance *L* calculated to be present from the spectrographic observations. Minimum daily doses of 100 γ of the most potent products (assumed from the degree of transformation of the ergosterol indicated by digitonin precipitation to be 50 per cent vitamin) cured rachitic rats in two weeks.

In their short wave-length experiments they employed a mercury argon source, operated to give chiefly an intense mercury resonance line at 2537A, with two filters, which transmitted most of the energy of this line. One, a 2-cm. column of saturated chlorine vapor at 6 atmospheres, absorbed the longer wave-lengths. The other, a 0.5-cm. column of 0.5-per cent aqueous potassium nitrate absorbed wave-lengths shorter than 2410A. Under these conditions, it seemed that from the start secondary reactions occurred. The general change seemed to be at first an increased absorption throughout the entire spectrum, followed by a gradual diminution culminating in practically complete transparency after 330 minutes. The ratios of the extinction coefficients of the 14-, 60- and 135-minute samples appeared independent of the wave-length within a wide range and indicated that these curves are representative of various concentrations of a substance *S*. This was marked by absorption at 2800A. Upon further irradiation, it was converted into a practically transparent product. From a comparison of the absorptions of *S* and that of *L* of the long wave-length irradiation experiments, it was concluded that early in the irradiations by short wave-lengths substance *L* is mainly formed with but little of *S*. But the rate of destruction of *L* by the 2537A line was much greater than that of *S* so that the concentration of *L*, assumed to be the vitamin, never made a high percentage of the materials present during the short wave-length irradiation. It was suggested that the product of Webster and Bourdillon may have contained the *S* substance and that this was responsible for their absorption results.

That divergent results are obtainable by the use of different wave-lengths was also indicated by the work of Griffith and Spence,[69] who employed a monochromator. Ergosterol irradiated by wave-lengths 2650A and shorter, when fed at a level of 0.01 mg. per day, failed to cure rats in two weeks but was effective in four weeks. Samples irradiated with rays in the range 2650 to 3130A cured in two weeks. Samples irradiated by still longer wave-lengths did not become antirachitic.

In subsequent work by Bourdillon, Fischmann and Jenkins,[70] it was shown that solutions of ergosterol of low concentration required shorter periods of irradiation to attain the maximum absorption at 2800A than those of higher concentrations. This is in agreement with the results of other photochemical changes outlined in the second section of this book. They also showed that when the radiations shorter than 2650A were filtered out the formation of the substance absorbing at 2800A was lessened, as had been shown by the Dutch workers, in the case of their substance *S*. They later agreed[71] that the substance with marked absorption between 2700 and 2800A is not the vitamin. They were able to obtain preparations of high potency but low absorption at 2800A. Lahousse and Gonnard[72] agreed in general with the results of Reerink and van Wijk. They found in the best products absorption at 2570 and probably also at 2690A but did not regard this product as the pure vitamin. It was also shown that even the substance *L* of Reerink and van Wijk was not a pure compound, two or more products being produced, probably in the same ratio in its formation. Some doubt was cast for a time upon the view that the vitamin has absorption at 2650A by the work of Ender,[73] who claimed that a very potent concentrate of the natural vitamin from tuna fish liver oil showed no selective absorption, a claim which has recently been shown erroneous.

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[68] See Everse, J. W. R., and van Niekerk, J., *Nederland Tijdschr. Geneesk.*, **75**, 1101 (1931); *Chem. Abs.*, **26**, 1010 (1932).

[69] Griffith, H. D., and Spence, K. C., *Brit. J. Actinotherapy*, **3**, 69 (1928).

[70] Bourdillon, R. B., Fischmann, C., and Jenkins, R., *Proc. Roy. Soc.*, **104B**, 561 (1929).

[71] Bourdillon, R. B., Jenkins, R., and Webster, T. A., *Nature*, **125**, 625 (1930).

[72] Lahousse and Gonnard, *J. phys. radium*, (6) **10**, 114S (1929).

Reerink and van Wijk[74] also observed that during the long-wave irradiation of ergosterol the optical rotation showed a linear dependence on the degree of transformation of the ergosterol. This they regarded as supporting the view that under their conditions but one product, the vitamin, is formed from ergosterol. This contrasted with the view of Askew, Bourdillon, Bruce, Jenkins and Webster,[75] who had obtained small amounts of a crystalline product with absorption maximum at 2680A, that the effect of long-wave irradiation is to produce simultaneously two substances, only one being the vitamin. Van Wijk, Reerink and Mörikofer[76] believed from absorption studies alone that the vitamin was more completely destroyed by prolonged exposure to sunlight than to the long-wave ultraviolet rays of the filtered mercury arc, a result they attributed to a difference in the distribution of energy from the two sources. Windaus[77] pointed out that long exposures to the magnesium spark are required to over-irradiate the vitamin, which he found to have a negative optical rotation and, from the observations of Holtz in his laboratory, to have an absorption maximum at about 2700A. It was also clear to Windaus that five or six irradiation products, all non-precipitable by digitonin, may form during the irradiation of ergosterol.[78] Haman and Steenbock[79] believe that the absorption at 2650A cannot be used as an accurate measure of the amount of the vitamin formed since the change is so complex.

Quantum Yields. During the period in which the emphasis was upon the spectrographic changes, little attempt was made to bring the principles of photochemistry to bear upon the problem. Some, such as Schlutz and Morse,[80] crudely conceived the irradiated material to be merely a storehouse of radiant energy which was later supposed to be reëmitted within the body, producing a sort of internal irradiation. Nevertheless, a few physical chemists made attempts (somewhat premature in view of the state of knowledge of the mechanism of the processes involved) to learn something of the amounts of energy required for the conversion of ergosterol or unpurified cholesterol into the vitamin. Fosbinder, Daniels and Steenbock[81] measured the ergs of the radiation 2650A required to produce a definite antirachitic potency in cholesterol and found the value to correspond to that in 3.2×10^{13} quanta. This was the energy required to produce a minimal threshold action. An attempt was made to calculate from this the least effective dose of the vitamin, the following assumptions being involved:

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[73] Ender, F., *Z. Vitaminforschung*, **2**, 241 (1933); *Brit. Chem. Abs.*, **A**, 1340 (1933); *Chem. Abs.*, **28**, 4103 (1934).

[74] Reerink, E. H., and van Wijk, A., *Biochem. J.*, **25**, 1001 (1931).

[75] Askew, F A., Bourdillon, R. B., Bruce, H. M., Jenkins, R. G. C., and Webster, T. A., *Proc. Roy. Soc.*, **107B**, 76, 91 (1930); Bourdillon, R. B., Jenkins, R. G. C., and Webster, T. A., *Nature*, **125**, 635 (1930).

[76] Van Wijk, A., Reerink, E. H., and Mörikofer, W., *Strahlentherapie*, **39**, 80 (1930-31); *Chem. Abs.*, **25**, 3034, 5692 (1931).

[77] Windaus, A., *Nachr. Ges. Wiss. Göttingen, Math. Physik Kl.*, 36 (**1930**); *Chem. Abs.*, **25**, 132 (1931).

[78] See also Holtz, F., *Strahlentherapie*, **34**, 637 (1929).

[79] Haman, R. W., and Steenbock, H., *Wis. Agr. Exp. Sta. Bull.*, **430**, 136 (1935); *Chem. Abs.*, **30**, 3472 (1936); *cf.* Fuchs, L., *Pharm. Presse Wiss.-Prakt. Heft*, 93 (**1933**); *Chem. Abs.*, **27**, 5478 (1933).

[80] Schlutz, F. W., and Morse, M., *Am. J. Diseases of Children*, **30**, 199 (1925).

[81] Fosbinder, R. J., Daniels, F., and Steenbock, H., *J. Am. Chem. Soc.*, **50**, 926 (1928).

(a) that the molecular weight of the vitamin is the same as that of cholesterol, (b) that the Einstein photochemical equivalence law applies and (c), although this was not recognized to be an assumption at the time, that no other simultaneous photochemical process occurs and that there is no loss of energy in any overirradiation destroying the vitamin. The calculation indicated that the vitamin should be active in doses of 0.02γ. For the irradiation of ergosterol, the value was given as 0.06γ.[82] Shortly after this, Coward[83] found the best preparation then available to give a positive result in the line test, a biological assay, in daily doses of 0.02γ, a result which appeared a remarkable confirmation of the physicochemical predictions. By extending the results to three other wavelengths, 2560, 2800 and 2930A, it was found that the results were independent of the wave length, the same dosage being arrived at in each case. In these irradiations only very short exposures were employed to eliminate the possibility of a loss of energy in overirradiation. As a result of this work the quantum efficiencies were thought to be independent of the wave-length, and, from other experiments, of the state of the ergosterol, *e.g.*, as solid or in solution (and in the latter case of the concentration of the solution) At present, it would seem very unlikely that a quantum yield of unity logically could have been assumed for photochemical reactions of such complexity occurring in condensed phases and, indeed, Kon himself has stated that the process is probably one with a low quantum yield. An approximation of the quantum yields actually

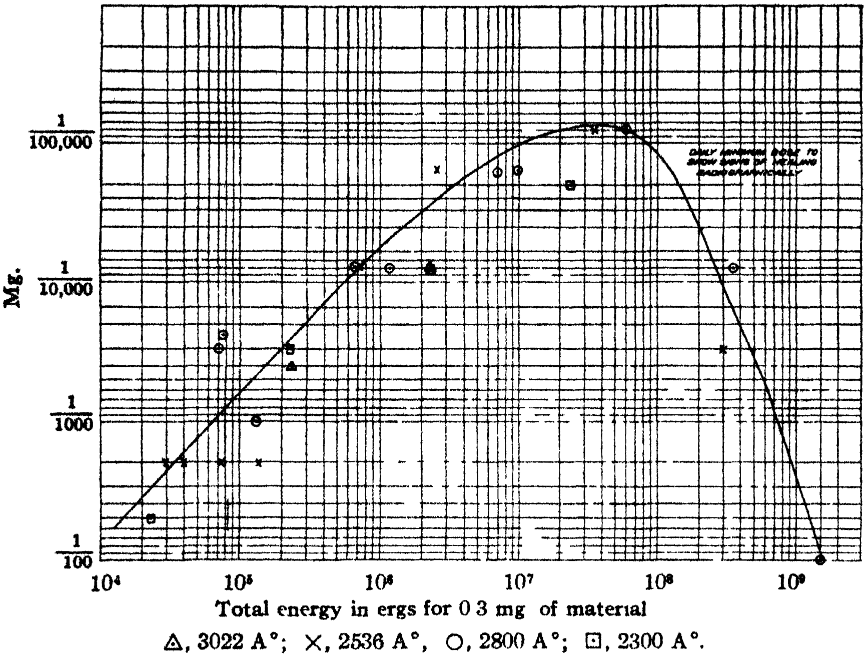

FIGURE 155. Amounts of Energy Required to Render Ergosterol Antirachitic (Marshall and Knudson, *Journal American Chemical Society*).

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[82] Kon, S. K, Daniels, F, and Steenbock, H, *J. Am. Chem. Soc.*, **50**, 2973 (1928).

[83] Coward, K. H., *Biochem. J.*, **22**, 1221 (1928).

obtained in these experiments is to be obtained by dividing the minimal dose (probably 0.03γ) of the more recent crystalline D_2 of Windaus and others by the calculated doses of Daniels (0.06γ). This gives a quantum yield of 0.5, still a remarkable agreement in view of the many assumptions involved. This work was extended by Marshall and Knudson[84] who plotted on log-log paper the minimum daily doses required to cure rats in three weeks which could be imparted to 0.3 mg. samples of ergosterol when irradiated by different amounts of energy at given wave-lengths. (See Figure 155). It was found that during the initial stages of irradiation the amount of the vitamin formed was directly proportional to the energy absorbed, since the minimum dose varied inversely with the ergs absorbed. For longer periods of irradiation, this relation failed, the net amount of the vitamin formed being smaller at each succeeding period until a stage was reached in which prolonged irradiation led to a loss in the vitamin previously produced. Thus these experiments yielded an independent confirmation of the results of spectrographic determinations. They calculated quantum yields of 0.3 to 0.2, based upon the potencies of the best preparations then available, those of Bourdillon and Webster. That this is greater than that of the D_2 mentioned in connection with the results of Daniels may account for the somewhat lower quantum yields of Marshall and Knudson. In two instances in which prolonged irradiations were made, the results with the 2536 and 2800A lines appeared to be identical. This result is hard to reconcile with the observations of Reerink and van Wijk.

OTHER FEATURES OF THE IRRADIATION CHANGES

During this period a number of other observations tended to throw some light on the influence of various factors on the irradiation process. The discovery that the irradiation could be effected successfully at −183°C., a temperature at which most bimolecular reactions are markedly inhibited, suggested the likelihood that the reaction is a monomolecular process, probably an isomerization.[85] The process is markedly affected by the choice of solvent.[86] In ether, the maximum potency is about five times that which can be attained in alcohol. The maximum is reached in 27 minutes in alcohol but only after four hours in ether. The vitamin is destroyed much more slowly by overirradiation in ether. Cyclohexane as solvent is intermediate between alcohol and ether. The vitamin can be destroyed by x-rays.[87]

During the early studies attempts were made to render unpurified cholesterol antirachitic by the action of x-rays. Hess and Weinstock[88] were unable in this way to alter its absorption spectrum, but Roffo and Correa[89] found that it was thereby rendered nonprecipitable by digitonin. Reinhard and Buchwald[90] found the absorption to be shifted to longer wave-lengths by x-rays or γ-rays, although the change in optical rotation was but slight. No antirachitic potency was acquired, according to Stenstrom, Lohmann and Hillstrom.[91]

Knudson[92] found commercial cholesterol could be rendered antirachitic by the

[84] Marshall, A. L., and Knudson, A., *J. Am. Chem. Soc.*, **52**, 2304 (1930).

[85] Bills, C. E., and Brickwedde, F. G., *Nature*, **121**, 452 (1928).

[86] Bills, C. E., Honeywell, E. M., and Cox, W. M., Jr., *J. Biol. Chem.*, **92**, 601 (1931).

[87] Morrison, R. R., Peacock, P. R., and Wright, S., *Biochem. J.*, **22**, 1138 (1928); Sumi, M., *Bull. Inst. Phys. Chem. Research, (Tokyo)* **8**, 640 (1929); *Chem. Abs.*, **25**, 1875 (1931).

[88] Hess, A. F., and Weinstock, M., *J. Biol. Chem.*, **64**, 181 (1925).

[89] Roffo, A. H., and Correa, L. M., *Boll. Inst. Med. Exptl., No. 5* (1925); *Brit. Chem. Abs.*, **A**, 523 (1929).

[90] Reinhard, M. C., and Buchwald, K. W., *J. Biol. Chem.*, **73**, 383 (1927).

[91] Stenstrom, W., Lohmann, A., and Hillstrom, H. T., *Proc. Soc. Exptl. Biol. Med.*, **25**, 817 (1928).

[92] Knudson, A., *Science*, **66**, 176 (1927); Knudson, A., and Coolidge, W. D., *Proc. Soc. Exptl. Biol. Med.*, **24**, 366 (1927).

action of cathode rays. Hieger believed that[93] cholesterol could be made activatable by x-rays only in the presence of a chlorine-containing solvent.

Ergosterol can be rendered active by cathode rays, but the activity attainable is only 0.04 that attainable by the use of ultraviolet rays.[94] That soft x-rays may be employed for the formation of the vitamin has been observed by Delaplace and Rebière[95] and by Loofbourow and Shelow.[96] The glow discharge has been successfully employed by Askew, Bourdillon and Webster.[97] The claim of Takamiya[98] that ozone is able to effect the production of the vitamin is apparently incorrect in view of the work to be described in a subsequent section which shows that ozone would completely destroy features of molecular structure upon which the vitamin action depends.

Even before the isolation of crystalline irradiation products, it appeared likely that the change involved in the production of the vitamin is one of isomerization. Early suggestions of a correlation between the peroxide content of antirachitic products and their potency[99] did not prove significant. That oxygen is not essential to the occurrence of the desired change in ergosterol is apparent from the many investigations in which it was excluded without affecting the process.[100] Nevertheless, it was possible before the structural formula of the sterols was as well understood as at present, to conceive of a secondary alcohol group being converted into a ketone by a migration of hydrogen atoms to some double bond.[101] Heilbron, Morton and Sexton[102] tended to favor a ketone structure for the vitamin, particularly because of the results of studies of the monomolecular spreading on water of films[103] of the irradiation products in comparison with the types of spreading exhibited by various sterol derivatives. However, many arguments were quickly marshalled against this possibility. In the first place, since ergosteryl acetate can acquire vitamin properties, it is unlikely that the hydroxyl groups can be affected.[104] Infrared absorption studies[105] indicated the persistence of the alcohol group and the non-appearance of a ketone group during the irradiation, except possibly in over-irradiated products. This was in agreement with the conclusions of Windaus and Linsert[106] from chemical evidence. It was stated that the optical activity changes from about −100° to +15° in 45 hours, but that the molecular weight remains unchanged and a free hydroxyl group remains as shown by the action of methyl magnesium iodide. Hydrogenations and perbenzoic acid titrations of the best products then available appeared to indicate that the number of double bonds remains unaltered. (This was later shown to have been in error.) This stimulated a number of investigations regarding the possible potency or activatability of the various chemically prepared isomers of ergosterol in which the positions of the double bonds are shifted, as well as that of the stereoisomers.[107]

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[93] Hieger, I., *Biochem. J.*, **21**, 407 (1927).

[94] Knudson, A., and Moore, C. N., *J. Biol. Chem.*, **81**, 49 (1929), see also Hoffman, R M, and Daniels, F., *J. Biol. Chem.*, **115**, 119 (1936).

[95] Delaplace, R., and Rebière, G., *Compt. rend.*, **188**, 1169 (1929)

[96] Loofbourow, J. R., and Shelow, E., *Bull. Basic Sci. Research*, **3**, 47 (1931).

[97] Askew, F. A., Bourdillon, R. B., and Webster, T. A., *Biochem. J.*, **26**, 814 (1932).

[98] Takamiya, E., *Bull. Agr. Chem. Soc. Japan*, **5**, 72 (1929); *Chem. Abs.*, **25**, 536 (1931); *J. Dept. Agr. Kyushu Imp. Univ.*, **3**, 1 (1930); *Chem. Abs*, **25**, 1877 (1931).

[99] Yoder, L., *J. Biol. Chem.*, **70**, 297 (1926); Schimkus, B., *Arch. Exptl. Path. Pharmakol.*, **121**, 230 (1927); *Chem. Abs.*, **21**, 2335 (1927); Rousseau, E., *Compt rend. soc. biol.*, **99**, 1844 (1928).

[100] See Beard, H. H., Burke, R. E., Thompson, H. E., and Goldblatt, H., *J. Biol. Chem.*, **96**, 307 (1932).

[101] See Windaus, A., and Linsert, O., [*Annalen*, **465**, 148 (1928)] for an early discussion of the chemical possibilities.

[102] Heilbron, I. M., Morton, R. A., and Sexton, W. A., *J. Chem. Soc.*, 47 (**1928**); Sexton, W. A., *Biochem. J.*, **22**, 1133 (1928).

[103] Rosenheim, O., and Adam, N. K., *Proc. Roy. Soc.*, **105B**, 422 (1929); Steigmann, A., [*Kolloid Z.*, **45**, 165 (1928); *Chem. Abs.*, **22**, 3432 (1928)] favored a ketone structure because of a color test.

[104] Heilbron, I. M., *Brit. J. Actinotherapy*, **2**, 210 (1928).

[105] Shelow, E., *Bull. Basic Sci. Res.*, **3**, 175 (1931); see also Hirsch, W., and Kellner, L., *Klin Wochschr.*, **10**, 171 (1931); *Chem. Abs.*, **25**, 2173 (1931); *Biochem. Z.*, **235**, 162 (1931).

[106] Windaus, A., and Linsert, O., *Annalen*, **465**, 148 (1928); Windaus, A., Westphal, K., von Werder, F., and Rygh, O., *Nachr. Ges. Wiss. Göttingen, Math. Physik Kl.*, 45 (**1920**); *Chem. Abs.*, **24**, 4799 (1930); Windaus, A., *Nachr. Ges. wiss. Göttingen, Math. Physik Kl.* 36 (1930).

ISOLATION OF CRYSTALLINE IRRADIATION PRODUCTS

Attention was diverted to the study of crystalline irradiation products which were isolated about 1930. There were a few earlier observations. Jendrassik and Keményffi[108] claimed the isolation of a crystalline substance effective in a daily dose of 0.01γ. This may be doubted since the product was said to exhibit no ultraviolet absorption spectrum and since the activity claimed exceeds that of the well-characterized products later obtained by others.* The first definitely characterized crystals, isolated by Windaus, Gaede, Köser and Stein,[109] proved to be biologically inactive as a result of over irradiation (50 hours). They could be separated into two fractions by fractional crystallization of the allophanate from benzene. As an indication of the excessive irradiation employed, they were called suprasterols I and II. Neither showed absorption of wave-lengths longer than 2500A. They were not precipitated by digitonin and were not mutually interconvertible. Suprasterol I melted at 104°C. and II at 110°C. They appeared to be triply unsaturated monohydric alcohols.

Active crystals were obtained shortly after this by Askew, Bourdillon, Bruce, Jenkins and Webster.[110] Ergosterol in ether solution was irradiated by a mercury-vapor lamp while flowing through a quartz tube at such a rate that about 40 per cent of the ergosterol was altered. After removal of the unchanged sterol by digitonin precipitation, the solution was evaporated *in vacuo* to a dry resin. By distillation at pressures between 0.002 and 0.01 mm. there were obtained distillates which, on solution in alcohol with water added formed just opalescent liquids. These mixtures, on slow evaporation in a vacuum desiccator, gave crystals melting 113-115°C. The ultraviolet absorption of these crystals agreed with that of the substance *L* of Reerink and van Wijk and in several samples the absorption paralleled the biological activity. The crystals were at first thought to be a mixture of two or more very similar substances (only one of which might be the vitamin), or else mixtures of antirachitic substances of different degrees of potency.

It was shown that a product prepared by irradiation with longer wave-lengths suffered a change on subsequent irradiation by shorter wave-lengths (2100-2800A), the absorption increasing at 2800A and the antirachitic value falling. On the other hand, irradiation by long wave-lengths for fifteen minutes had but little effect on the antirachitic potency. It was suggested, from closer analysis of the results, that the inactive substance absorbing at 2800A is produced during the re-irradiation of the long wave-length product by short wave-lengths, not from the vitamin but from some other substance present, to an extent which depends upon the conditions used in the first irradiation. They did not believe this to be a precursor of the vitamin but some other substance formed simultaneously with it. The simultaneous production of two products, one of which is inactive, would prevent the concentration of the vitamin produced by irradiation from ever reaching 100 per cent. Within a year they had improved the technique[111] to an extent that permitted the preparation of several grams of the crystals. In this process, it was essential that oxygen be excluded. The oxygen uptake of the irradiated products was thought to be largely due to the oxidation of products other than the vitamin for much oxygen could be absorbed without a corresponding loss of potency. Provisionally, they gave the name *calciferol* to the crystals, recognizing the possibility that they might not be a single compound. This substance melted at 123-125°C. and had $[\alpha]^{5461}_{20°}=+260°$. The absorption spectrum showed a maximum at 2700A and an inflection at 2600A indicative of a second maximum. The elementary analysis and molecular weight determination indicated the substance to be an isomer (or a mixture of isomers) of ergosterol. Partially successful esterifications indicated the presence of an alcohol group. They were then uncertain as to whether the calciferol was a product of the original irradiation or one which had been altered by the heat employed in the subsequent distillation. The purity of these calciferol crystals was questioned by Bills, McDonald, Be Miller, Steel and Nussmeier.[112]

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[107] Bills, C. E., and Cox, W. M., Jr., *J. Biol. Chem.*, **84**, 455 (1929); Bills, C. E., Cox, W. M., Jr., and Steel, G. E., *Ibid.*, **84**, 655 (1929); MacCorquodale, D. W., Steenbock, H., and Adkins, H., *J. Am. Chem. Soc.*, **52**, 2512 (1930); Hart, M. C., and Heyl, F. W., *Ibid.*, **52**, 2013 (1930); Emerson, H., and Heyl, F. W., *Ibid.*, **52**, 2015 (1930); Hart, M. C., Speer, J. H., and Heyl, F. W., *Ibid.*, **52**, 2016 (1930); Heilbron, I. M., Johnstone, F., and Spring, F. S., *J. Chem Soc.*, **2248** (**1929**); Windaus, A., and Auhagen, E., *Annalen*, **472**, 185 (1929); Windaus, A., Dithmar, K., Murke, H., and Suckfüll, E., *Annalen*, **488**, 91 (1931); Cox, W. M., Jr., and Bills, C. E., *J. Biol. Chem.*, **88**, 709 (1930); Natelson, S., Sobel, A. E., and Kramer, B., *Ibid*, **105**, 761 (1934); Natelson, S., and Sobel, A. E., *Ibid.*, **109**, 687 (1935).

[108] Jendrassik, A., and Keményffi, A. G., *Biochem. Z.*, **216**, 238 (1929).

* Reerink and van Wijk, it may be recalled, stated that they had evidence of crystals at low temperatures in their products.

[109] Windaus, A., Gaede, J., Köser, J., and Stein, G., *Annalen*, **483**, 17 (1930).

[110] Askew, F. A., Bourdillon, R. B., Bruce, H. M., Jenkins, R. G. C., and Webster, T. A., *Proc. Roy. Soc.*, **107**, 76, 91 (1930).

Meanwhile at Göttingen crystals were also obtained and called D_1.[113]

The irradiation products obtained under conditions of little or no overirradiation, after being freed from unchanged ergosterol, were allowed to react with citraconic anhydide at room temperature. That portion which had reacted was removed after three days and the solvent evaporated from the remainder. The residue could be easily recrystallized, as long needles melting at 124-5°C. and subliming in high vacuum at 135°C. They had an absorption band with a maximum at 2650-2700A and were isomeric (composition and molecular weight) with ergosterol. The limiting antirachitic dose was 0.025γ. The crystals had a high positive rotation, in acetone or alcohol, $[\alpha]^{5461}_{20°}=+171°$ Samples made by the method of Reerink and van Wijk, however, showed a specific rotation of but +30°. D_1 seemed, furthermore, different from the crystals obtained in England since after ten recrystallizations, the German product had a rotation of +159° and the English of +260°. Windaus suggested that it might be that the only change involved was a steric one leading to an increase in the spatial size of the molecule. But it was suggested that during overirradiation, the double bonds which form a conjugated system may be moved to positions further apart.[114] The combination of the crystals with maleic anhydride indicated the presence of a conjugated double bond. At room temperature the new crystals absorbed no oxygen in twelve hours.

It was soon found, however, that neither calciferol nor D_1 represented the pure antirachitic photoisomer of ergosterol. The English workers announced that[115] by fractional crystallization of the 3,5-dinitrobenzoate, their product had been separated into an inactive substance, pyrocalciferol, formed by the action of heat during the distillation, and the true antirachitic compound, for which they retained the name calciferol. Thus their original or "old calciferol" had been calciferol contaminated with pyrocalciferol, which is again an isomer.

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[111] Angus, T. C., Askew, F. A., Bourdillon, R. B , Callow, R. K., Fischmann, C., Philpot, J., and Webster, T. A., *Ibid,* 108B, 340 (1931).

[112] Bills, C. E., McDonald, F. G., Be Miller, L. N., and Nussmeier, M., *J. Biol. Chem.*, 93, 775 (1931).

[113] Windaus, A., Lüttringhaus, A., and Deppe, M., *Annalen*, 489, 252 (1931); Windaus, A., *Proc. Roy. Soc.*, 108B, 568 (1931).

[114] For evidence for this from refractive indices, see Von Auwers, K., and Wolter, E., *Nachr. Ges. Wiss. Göttingen, Math. Physik. Kl.*, 101 (1931); *Chem. Abs.*, 26, 5844 (1932).

[115] Askew, F. A., Bruce, H. M., Callow, R. K., Philpot, J. St. L., and Webster, T. A., *Nature*, 128, 758 (1931).

Windaus and Linsert, in a brief note,[116] announced the isolation of another compound, D_2 melting at 115-116°C. and having $[\alpha]_D = +85°$ in acetone. This was obtained by the dinitrobenzoate method from D_1 which was found to consist of D_2 and an isomeric alcohol.[117] D_2 also shows definite absorption at 2650A. New calciferol and D_2 are identical, but the old calciferol and D_1 were not. The former had as the second material pyrocalciferol (and probably also the contaminant of D_1) and the latter had as the second component an isomeric alcohol formed from ergosterol by irradiation.[118] This has been called lumisterol, or a sterol formed by light. The lumisterol has its absorption maximum at about 2700A and is the substance which, on irradiation with short wave-lengths, is converted to the substance with strong absorption at 2800A. It was readily shown that lumisterol and calciferol (D_2) in equimolar proportions would have the absorption spectrum of D_1. The English workers suggested that the substance *L* of Reerink and van Wijk may have been a mixture of calciferol (D_2) and one or more inactive irradiation products. It was next shown by Windaus, Dithmar and Fernholz,[119] by titrations with perbenzoic acid, that lumisterol contains three double bonds. It has no antirachitic action and is not toxic. By irradiation in ether with the unfiltered light from a magnesium arc, in which the longer rays predominate, it is converted, in part at least, into D_2. Thus it must be a transitory intermediate product in the conversion of ergosterol into D_2. From the English observations, it would seem that, if in this process the lumisterol is irradiated by too short wave-lengths, the reaction follows a different course, producing the substance which absorbs maximally at 2800A. That the substance which disappears when this absorption at 2800A is produced is not the vitamin had been shown previously by Windaus and Auhagen.[120]

It was not yet apparent why it was so necessary to eliminate oxygen during the irradiation since none of the products thus far described is readily attacked by it. It was believed both by Windaus and by the English group that the irradiation product attacked by oxygen is not the antirachitic material. In further studies, Windaus, von Werder, and Lüttringhaus[121] isolated a substance from the treatment of the irradiation product with citraconic anhydride. Because of the rapidity with which it reacts with that reagent (much greater than D_2) it was called tachysterol. Since it reacts rapidly with oxygen also, it seems to be the product which makes the exclusion of oxygen essential. That this material must be preserved in order to secure high yields of D_2 during irradiation seems to imply that it lies in the direct line of conversion of ergosterol into D_2.[122] Tachysterol lacks antirachitic action and is not toxic.

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[116] Windaus, A., and Linsert, O., *Annalen*, **489**, 269 (1931); see also *Z. physiol. Chem.*, **203**, 70 (1931).

[117] This work has been reviewed by Lüttringhaus, A., *Chem. Ztg.*, **55**, 956 (1931).

[118] Detailed accounts of the preparation of new calciferol are given in *Proc. Roy. Soc.*, **109B**, 488 (1932) and of D_2 by Windaus, A., Linsert, O., Lüttringhaus, A., and Weidlich, G., *Annalen*, **492**, 226 (1932). For criticism, see Bills, C. E., and McDonald, F. G., *J. Biol. Chem.*, **96**, 189 (1932). For another method of obtaining the crystals, see Sumi, M., *J. Agr. Chem. Soc. Japan*, **12**, 1211 (1936); *Bull. Inst. Phys. Chem. Research (Tokyo)*, **15**, 635 (1936); *cf.* also Francesconi, L., and Opisso, F., *Ann. chim. appl.*, **25**, 124 (1935); *Brit. Chem. Abs.*, **A**, 857 (1935); *Chem. Abs.*, **29**, 6254 (1935).

[119] Windaus, A., Dithmar, K., and Fernholz, E., *Annalen*, **493**, 259 (1932).

[120] Windaus, A., and Auhagen, E., *Z. physiol. Chem.*, **196**, 108 (1931).

[121] Windaus, A., von Werder, F., and Lüttringhaus, A., *Annalen*, **499**, 188 (1932).

[122] Inhoffen, H. H., and Hauptmann, H., [*Z. physiol. Chem.*, **207**, 259 (1932)] believe that in the presence of tachysterol, D_2 becomes slightly sensitive to air.

It has a high absorption maximum at 2800 A and further bands at 2680 and 2940A and is changed, in part at least, into D_2 when irradiated by the magnesium spark. It thus appears to be the substance built up by short-wave irradiation of ergosterol or of lumisterol. That it does not appear during the long-wave irradiation is probably due to the fact that it is formed only in low concentrations and immediately converted into D_2. The use of short waves, owing to lack of absorption, could probably only very slowly convert it into D_2.

It thus became apparent that five isomers of ergosterol are produced by irradiation and it became possible to place them in the sequence in which the transformations occur.[123] Slight differences in the order were suggested in these papers, the following being the sequence of changes given in the most recent paper of Setz.

$$\begin{tikzcd}[row sep=small] & & & & \text{Suprasterol I} \\ \text{Ergosterol} \arrow[r] & \text{Lumisterol} \arrow[r] & \text{Tachysterol} \arrow[r] & D_2 \arrow[ur] \arrow[r] \arrow[dr] & \text{Suprasterol II} \\ & & & & \text{Substance 248} \end{tikzcd}$$

The substance 248 is so called because it has an absorption maximum at 2480A. It may be recalled that this substance was originally mistaken for the vitamin by Pohl. It is a product of overirradiation and is not antirachitic but is toxic and sometimes called toxisterol.[124] Setz states that irradiation of any substance in the list leads to the formation of a mixture of all substances following it, but that the sequence cannot be reversed. Light of the longest wave-length, 3100A, capable of altering ergosterol gives rise to lumisterol after which further change is but slow. With the use of somewhat shorter wave-lengths, 2800A, the lumisterol stage is passed over and tachysterol is immediately produced. It is very sensitive to longer wave-lengths and is converted into D_2. Between 3000 and 3600A, it absorbs more than ten times as strongly as does ergosterol. The existence of this sequence may explain why the mercury arc light, when freed by a xylene filter from rays shorter than 2800A, forms chiefly the vitamin and lumisterol in fairly constant proportions. The shorter rays are necessary to convert the lumisterol into tachysterol. The magnesium light, 2780 to 2800A, yields practically no lumisterol but chiefly tachysterol and D_2, suggesting that the tachysterol may be formed without passing through lumisterol as an intermediate stage. Against this possibly oversimplified scheme is also the fact that on short irradiations during which but 10 per cent of the ergosterol has been altered, D_2 predominates in the mixture, although it might be expected that the first product, lumisterol, would predominate. In a product of longer irradiation (method of Reerink and van Wijk) with 50 per cent ergosterol conversion, there were found to be present about 40-50 per cent of lumisterol, 30-40 per cent of D_2, 40-50 per cent of tachysterol, 5-10 per cent of suprasterol II and possibly also traces of suprasterol I.

By the use of a monochromator, Bowden and Snow[125] recently showed that calciferol in cyclohexane is rapidly decomposed by the wave-length 2650A, but is not changed by 3130A or longer wave-lengths. The decomposition is independent of the presence of air. Ergosterol in cyclohexane was not altered by the wavelength 3130A but was rapidly converted into calciferol by 2967A. With 2650A, the yield of calciferol was decreased. Thin crystals of ergosterol were scarcely affected by 3650, 3130 or 2537A, but were rapidly transformed by 2967A.

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[123] Windaus, A., Lüttringhaus, A., and Busse, P., *Nachr. Wiss Göttingen, Math. Physik Kl.* 150 (1932); *Chem. Abs.*, **27**, 2180 (1933); Windaus A., von Werder, F., and Lüttringhaus, A., *Annalen*, **499**, 188 (1932); Setz, P., *Z. physiol. Chem.*, **215**, 183 (1933).

[124] Laquer, F., and Linsert, O., *Klin. Wochschr.*, **12**, 753 (1933). Spectroscopic evidence by Dimroth indicates that ergosterol cannot form tachysterol without passing through lumisterol, *Ber.*, **70B**, 1631 (1937). See also Windaus, A., *Sitzber, preuss. Akad. Wiss. Physik-math. Kl., No. 9-12*, 104 (1937).

[125] Bowden, F. P., and Snow, C. P., *Proc. Roy. Soc.*, **115B**, 261 (1934).

Jendrassik[126] has claimed that ergosterol can be rendered antirachitic by irradiation with sunlight, yielding a preparation 2 per cent as potent as that produced by artificial ultraviolet sources. It has been found possible to irradiate ergosterol by ultraviolet rays which have passed through the epidermis of a day-old rat.[127]

Chemical Changes Occurring During the Irradiation of Ergosterol

It has been pointed out in the preceding discussion that the various irradiation products in the sequence of changes undergone by ergosterol are all isomers. The elucidation of the constitution of each of these, established in all of the most important features, has been accomplished by the application of chemical and physical methods. Among the physical methods have been the comparison of the data on ultraviolet absorption, refractive indexes and x-ray crystal structures of these products with those of related compounds of known constitution. The chemical attack has involved the identification of oxidation products, the determination of the number of double bonds in the various products by catalytic microhydrogenation methods and by perbenzoic acid titrations, and the determination of their conjugation by the maleic anhydride reaction. The number of rings present was found by selenium dehydrogenations followed by the identification of the products. Finally, the thermal decomposition products have been studied. The details of the historical development lie beyond the scope of this discussion.[128]

It was first shown that the double bond (C_{22} to C_{23}) in the side-chain is unaltered during the transformations, since ergosterol, lumisterol, tachysterol, D_2 and suprasterol I can each yield methylisopropylacetaldehyde on suitable treatment.[129] The changes must then be stereochemical or associated with the positions and stability of the double bonds within ring B of ergosterol.

Three double bonds were found present in lumisterol,[130] and studies of the oxidation products indicated them to be in substantially the same positions as in ergosterol, a result supported also by dehydrogenation experiments by Dimroth. Only a stereoisomeric change remains as a possibility.[131] This was at first thought to consist in an epimerization of the hydroxyl group at position 3, but this has been shown unlikely by the observation that the unsaturated hydrocarbons produced by the dehydration of ergosterol and lumisterol by phosphoryl chloride are different.[132] Dimroth[133] has shown by a comparison of the absorption spectra of dehydrolumisterol and dehydroergosterol, and by other chemical evidence, that the change in configuration occurs at the methyl group of C_{10}.[134] This persists in the succeeding products as well and Dimroth attributes the inability of the irradiation products to combine with digitonin to the spatial arrangement of the methyl group at C_{10} produced in the first transformation of the series.

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[126] Jendrassik, A., *Biochem. Z.*, **252**, 205 (1932).

[127] Lucas, N. S., *Biochem. J.*, **27**, 132 (1933).

[128] For detailed reviews, see Lettré, H., *Annalen*, **511**, 280 (1934); Callow, R. K., *Sci. J. Roy. Coll. Sci.*, **4**, 41 (1934); Rosenheim, O., and King, H., *Chem. & Ind.*, 196, **(1934)**; 699 (1935); Nicola, O., *Rev. Med. Latin-Am.*, **220**, 358 (1934); **231**, 279; *Chem. Abs.*, **29**, 8075 (1935); Linsert, O., *Med. Chem. Forschungstatten I. G. Farbenind.*, **2**, 281 (1934); Rygh, O., *Tids. Kjemi Bergvesen*, **14**, 26 (1934); Windaus, A., *E. Merck's Jahresber.*, **50**, 3 (1936); Ruzicka, L., and Goldberg, M. W., *Helv. Chim Acta*, **18**, 434 (1935); Schmidt, O., *Ber.*, **68B**, 1658 (1935); Heilbron, I. M., and Spring, F. S., *Chem. & Ind.*, 795 **(1935)**; *Current Sci.*, **5**, 69 (1936); Fieser, L. F., "Chemistry of Natural Products Related to Phenanthrene," Reinhold, 2nd ed., 177 (1937); Heilbron, I. M., *Chimie et industrie*, **39**, 19 (1938); Bills, C E., *J. Am. Med Assoc.*, **110**, 2150 (1938).

[129] Guiteras, A., *Annalen*, **494**, 116 (1932).

[130] Dimroth, K., and Möller, E. F., *Ber.*, **68B**, 539 (1935); Heilbron, I. M, Spring, F. S., and Stuart, P. A., *J. Chem. Soc.*, 1221 **(1935)**; Haslewood, G., and Roe, E., *J., Chem. Soc.*, 465 **(1935)**.

[131] More recent proof is due to Burawoy, A., *J. Chem. Soc.*, 409 **(1937)**, and Heilbron, I. M., Moffet, G. L., and Spring, F. S., *J. Chem. Soc.*, 411 **(1937)**.

[132] See, however, Callow, R. K., and Young, F. G., *Proc. Roy. Soc.*, **157A**, 194 (1936).

A most significant observation by Lettré[135] showed tachysterol to contain the equivalent of four double bonds.[136] This could result only from the opening of a ring, reducing the number of rings in the system from four to three. For a time it was believed that in the conversion of tachysterol to D_2 a fourth ring is reformed. Unfortunately, it was not possible to obtain crystalline dehydrogenation products which might yield information as to the number of rings. However, it was established that D_2 also contains four double bonds by hydrogenation and by perbenzoic acid titrations.[137] Müller showed that it contained three of its double bonds in a conjugated system and differed only from tachysterol in the location of these bonds. Rosenheim and King[138] were of the opinion that the breaking of the ring in tachysterol formation took place between C(5) and C(10), resulting in the unusual formation of a ten-membered ring. This view was based upon x-ray evidence of Bernal,[139] which appeared to indicate an essential similarity of the unit cells of all of the irradiation products, the length of the molecule not being affected by the intramolecular changes. Proof that this is incorrect and that it is the bond between positions 9 and 10 which is broken was furnished by Lettré and by Heilbron and Spring[140] by the study of the products of the oxidation of D_2. In this work it was established that there must be a double bond in calciferol between positions 5 and 6. Furthermore, Windaus and Thiele by a study of certain degradation products and their maleic anhydride addition compounds located the remaining double bonds so that the structure of D_2 is that represented below.[141]

The thermal decomposition products of the D_2, pyrocalciferol and isopyrocaliferol are formed by a process involving a ring closure,[142] since the equivalent of a double bond disappears. The process occurs in such a manner as to re-form the original sterol ring system. There is evidence that a ring closure occurs also in the formation of suprasterol I by overirradiation but a different ring system, possibly containing a spirocyclopentane ring, is formed.[143]

Pyrocalciferol irradiated forty hours with magnesium light in peroxide-free ether yields photopyrocalciferol, and isopyrocalciferol similarly gives a photoisopyrocalciferol. Such changes are due to the conjugated system of two double bonds between C_5 and C_6 and between C_7 and C_8 in ring B, found also

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[133] Dimroth, K., *Ber.*, **69**, 1123 (1936).

[134] Windaus, A., and Dimroth, K., *Ber.*, **70B**, 376 (1937).

[135] Lettré, H., *Annalen*, **511**, 280 (1934); *Angew Chem.*, **47**, 736 (1934).

[136] See also Kuhn, R., and Möller, E. F., *Angew. Chem.*, **47**, 145 (1934).

[137] Müller, M., *Z. physiol Chem.*, **233**, 223 (1935); Fernholz, E., *Annalen*, **499**, 198 (1932); Ahrens, G., Fernholz, E., and Stoll, W., *Ibid.*, **500**, 109 (1933); Heilbron, I. M., Samant, K. M., and Spring, F. S., *Nature*, **135**, 1072 (1935); Windaus, A., and Thiele, W., *Annalen*, **521**, 160 (1935).

[138] Rosenheim, O., and King, H., *Chem. & Ind.*, 699 (1935).

[139] Bernal, J. D., *Nature*, **129**, 277 (1932); Bernal, J. D., and Crowfoot, D., *Chem. & Ind.*, **54**, 701 (1935).

[140] Heilbron, I. M., and Spring, F. S., *Chem. & Ind.*, 795 (1935). The Windaus structures are corroborated by refractometric studies by von Auwers, K., [*Annalen*, **533**, 255 (1938)], as well as by other recent work of Heilbron, I. M., Kennedy, T., Spring, F. S., and Swain, G., [*J. Chem. Soc.*, 869 (1938)].

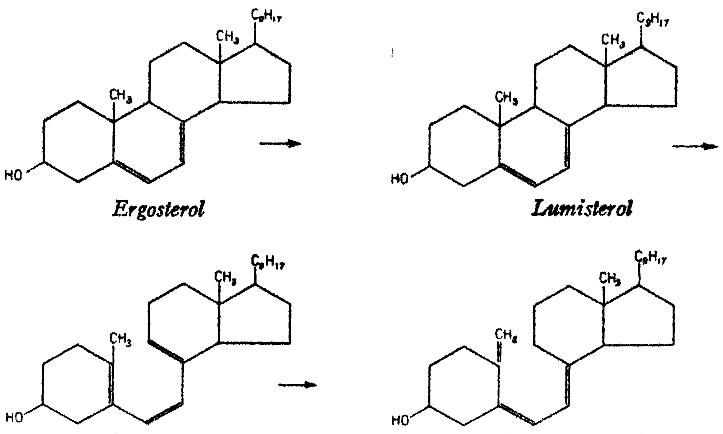
[141] See also Heilbron, I. M., Jones, R. N., Samant, K. M., and Spring, F. S., *J. Chem. Soc*, 905 (1936); Windaus, A., and Grundmann, W., *Annalen*, **524**, 295 (1936); von Reichel, S., and Deppe, M., *Z. physiol. Chem.*, **239**, 143 (1936).

[142] Busse, P., *Z. physiol. Chem.*, **214**, 211 (1933); Müller, M., *Ibid.*, **233**, 223 (1935).

[143] Müller, M., *Z. physiol. Chem.*, **233**, 223 (1935).

in ergosterol, 22-dihydroergosterol, 7-dehydrocholesterol and 7-dehydrositosterol. Pyrocalciferol and isopyrocalciferol differ from ergosterol and lumisterol in having a different steric arrangement at C_9. The irradiation of the pyro- compounds converts the conjugated system into a system of isolated double bonds, which may again be converted by heat into the original conjugated system. No steric rearrangement occurs at C_{10}. Instead, a double linkage is shifted from ring B to ring A.

Fuchs and van Niekerk[144] observed that crystalline D_2 kept in air in darkness undergoes some changes involving the development of a yellow color and the loss of ultraviolet absorption. Little is yet known regarding the structure of suprasterol II or of the substance 248 (toxisterol). The structures of the various irradiation products are summarized by the following formulas:



Ergosterol *Lumisterol*

Tachysterol D_2 (*Calciferol*)

The positions of the double bonds in tachysterol are perhaps still uncertain. If the conversion of this to vitamin D_2 is as indicated, it is conceivable that the absorption of light by tachysterol involves the liberation of atomic hydrogen which later adds on again at position 9. It would be interesting to learn whether its presence could be detected during the photochemical process by the aid of the para hydrogen conversion. Grundmann gives evidence for proposing that the double bonds in tachysterol should be placed as shown rather than in the positions 1,10; 5,6 and 7,8.[145]

Recently, attention has been paid to the effects of irradiation on the surface pressures and surface potentials of unimolecular films of ergosterol.[146] The evidence indicates a change in the shape of the molecules as the irradiation proceeds. The results were attained before the structures indicated above had been determined and they have not been correlated with them as yet.

There has not as yet been achieved a direct synthesis of D_2. Natelson and Gottfried, however,[147] have synthesized 4-β-phenylethylindane, the structure proposed for the calciferol nucleus.

[144] Fuchs, L., and van Niekerk, J., *Biochem. Z.*, **277**, 32 (1935).

[145] Grundmann, W., *Z. physiol. Chem.*, **252**, 151 (1938).

[146] Fosbinder, R. J., *Proc. Roy. Soc.* **139A**, 93 (1933); Danelli, J. F., and Adam, N. K., *Biochem. J.*, **28**, 1583 (1934).

[147] Natelson, S., and Gottfried, S. P., *J. Am. Chem. Soc.*, **58**, 1432 (1936).

The activation energy of the conversion of ergosterol into D_2 has recently been calculated from quantum mechanical considerations.[148]

The activation energy sets the long wave-length limit for the conversion. If there is merely the breaking of a C—H linkage on C_{18} followed by a migration of the hydrogen atom to the carbon in position 9, the activation energy is 92.3 kcal. which agrees well with the usually accepted long wave-length limit of about 3100A. The authors considered many other mechanisms and found the one involving the least energy of activation to require 72 kcal. which would place the long wave-length threshold at about 3950A. The suggested mechanism does not take into account the stereochemical change involved in the formation of lumisterol. It may be that this requires a somewhat greater energy of activation and sets the observed wave-length limit.

That a longer threshold than 3100A has not been experimentally observed may be due to the failure of ergosterol to absorb the longer wave-lengths. If this is the case and the mechanism postulated by Sherman is the actual one, it might be possible to effect the conversion in a sensitized process. There have been a number of observations of photochemical changes in ergosterol occurring in the presence of eosin and other sensitizers. The reactions observed, however, have been of an entirely different character.[149] The reaction is a photoöxidation, in which ergosterol peroxide is produced. The reaction is inhibited by potassium cyanide. Under similar conditions, ergosteryl acetate also yields a peroxide. The peroxides are biologically inactive. In the absence of oxygen, white light in the presence of a sensitizer causes a dehydrogenation of the sterol, and there results a sparingly soluble substance, $C_{56}H_{86}O_2$, known as ergopinacol, which is biologically inert. The study of these substances played a part in the development of the structural formula for ergosterol. Rygh[150] found that in the presence of eosin, sunlight causes a rearrangement of ergotetraene, melting at 97°C. to an isomeric form, of slighty lower optical rotation. No peroxide was formed even in the presence of air. Windaus and Langer[151] found that an alcoholic solution of 22-dihydroergosteryl acetate may be oxidized in the presence of eosin by a 500-watt lamp to a peroxide. The free 22-dihydroergosterol itself behaves similarly. Dimroth[152] also has shown that, in alcohol, dehydrolumisterol acetate reacts with eosin in sunlight to give a so-called pinacol, but that lumisterol and pyrocalciferol do not behave in this way. Dehydroergosterol acetate and isopyrocalciferol yield the same pinacol when treated in this manner. It differs from that[153] obtained from dehydrolumisterol.

According to Montignie[154] sunlight does not influence the reactions of cholesterol with uranyl nitrate, silver nitrate, mercury oxide, iodoform or mercuric iodide.

OTHER ANTIRACHITIC COMPOUNDS

Windaus and Langer[155] made the important observation that ergosterol in which the double bond in the side chain has been saturated, *i.e.*, 22-dihydroergosterol, can also function as a provitamin, although the antirachitic activity of the irradiation product is but one-thirtieth that of D_2. This means that the double bond in the side chain does not play a part in the sequence of irradiation changes in the case of ergosterol. This observation was made before the evidence presented in the preceding discussion of the mechanism of the formation of D_2.[156] It led to the suggestion that it might be possible to prepare an antirachitic substance from cholesterol could there first be introduced into the molecule a double bond in position 7, 8, thus rendering the molecule analogous to that of ergosterol in the features essential to the conversion. This was accomplished by Windaus, Lettré and Schenck,[157] who succeeded in preparing the benzoate of 7-dehydrocholesterol. The product of its irradiation even in a crude form had a high antirachitic potency, approximately half that of the product from ergosterol. This work provided a justification of the objections that had been raised by a relatively few earlier workers to the almost universally accepted view that ergosterol was the precursor of the vitamin D.

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[148] Owen, J. R., and Sherman, A., *J. Am. Chem. Soc*, **59**, 763 (1937)

[149] Windaus, A., Borgeaud, P., and Brunken, J., *Nachr Ges. Wiss. Göttingen, Math. Physik Kl.*, 313 (1927); Windaus, A., and Brunken, J., *Annalen*, **460**, 225 (1928); Windaus, A., and Borgeaud, P., *Annalen*, **460**, 235 (1928); compare Meyer, K., *J. Biol. Chem.*, **103**, 607 (1933).

[150] Rygh, O., *Z. physiol. Chem.*, **185**, 99 (1929).

[151] Windaus, A., and Langer, R., *Annalen*, **508**, 105 (1933).

[152] Dimroth, K., *Ber.*, **69B**, 1123, 1631 (1936).

[153] Windaus, A., and Dimroth, K., *Ber.*, **70B**, 376 (1937).

[154] Montignie, E., *Bull. Soc. Chim.*, **1**, 290 (1934); *Chem. Abs.*, **28**, 5466 (1934).

[155] Windaus, A., and Langer, R., *Annalen*, **508**, 105 (1933).

Jendrassik and Kemenyffi[158] had been of the opinion that a removal of the provitamin from a cholesterol preparation destroys an equilibrium between cholesterol and a provitamin leading to the conversion of more cholesterol into provitamin. They had no conception of the nature of the provitamin but suggested that it might be ergosterol. Bills, Honeywell and MacNair[159] maintained that samples of cholesterol contained traces of an activatable substance other than ergosterol, a view not shared by Kon, Daniels and Steenbock.[160] Koch, Koch and Ragins[161] asserted that even purified cholesterol could to a slight extent be activated and that it might be made more activatable by heating it slightly above the melting point. Koch, Koch and Lemon[162] concluded from spectrographic studies that ordinary cholesterol contains only about one-thousandth part of ergosterol[162a] but was more capable of activation than could be accounted for by this ergosterol, so that some other activatable substance must be present. At the time, these views attracted relatively little attention. Yoder[163] has recently called attention to a chemical method of obtaining antirachitic material from cholesterol by means of sulfur trioxide and acetic anhydride. DeCaro[164] claimed the non-saponifiable fraction of lanolin acquires antirachitic properties on irradiation. Gustavson[165] found that the extraction of irradiated cholesterol with liquid ammonia gave a yellow resinous material a quarter of a milligram of which gave complete protection against rickets when incorporated in the McCollum rachitic diet.

The brilliant results of the ergosterol investigations diverted attention from cholesterol and it came to be rather generally believed that D_2 was identical with the vitamin from natural sources. This view was maintained until an interesting difference in the response of rachitic animals of different species to the action of the antirachitic vitamin from various sources showed the non-identity of D_2 with the natural vitamin of cod-liver oil.[166] Hess and Supplee[167] observed that chickens are regularly protected against leg weakness by the addition of

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[156] The product has recently been isolated through the nitrobenzoate as crystalline D_4., Windaus, A., and Trautmann, G., *Z. physiol. Chem.*, **247,** 185 (1937).

[157] Windaus, A., Lettré, H., and Schenck, F., *Annalen*, **520,** 98 (1935).

[158] Jendrassik, A., and Kemenyffi, A. G., *Biochem. Z*, **189,** 180 (1927); **201,** 269 (1928).

[159] Bills, C. E., Honeywell, E. M., and MacNair, W. A., *J. Biol. Chem.*, **76,** 251 (1928).

[160] Kon, S. K., Daniels, F., and Steenbock, H., *J. Am. Chem. Soc.*, **50,** 2573 (1928).

[161] Koch, F. C., Koch, E. M., and Ragins, I. K., *J. Biol. Chem.*, **85,** 141 (1929).

[162] Koch, F. C., Koch, E. M., and Lemon, H. B., *J. Biol. Chem.*, **85,** 159 (1929).

[162a] Actually 7-dehydrocholesterol has a similar absorption spectrum.

[163] Yoder, L., *J. Biol. Chem.*, **116,** 71 (1936); Eck, J. C., Thomas, B. H., and Yoder, L., *Ibid.*, **117,** 655 (1937); Eck, J. C., and Thomas, B. H., *Ibid.*, **119,** 621 (1937)

[164] De Caro, M., *Boll. soc. ital. biol. sper.*, **7,** 1097 (1932); *Chem. Abs.*, **27,** 1035 (1933).

[165] Gustavson, R. G., *J. Colorado-Wyoming Acad. Sci*, **1,** 23 (1929); *Chem. Abs.*, **26,** 3547 (1932).

[166] This work was reviewed by Holmes, A. D., *New England J. Med.*, **204,** 211 (1931); *Chem. Abs.*, **26,** 179 (1932).

[167] Hess, A. F., and Supplee, G. C., *Proc. Soc. Exptl. Biol. Med.*, **27,** 609 (1930).

1 per cent of cod-liver oil to their rations. A supplement of irradiated ergosterol equivalent in rat experiments to many times this amount of vitamin D failed, however, to afford protection. In experiments on White Leghorns, Massengale and Nussmeier[168] found it necessary to administer a quantity of irradiated ergosterol equivalent by rat assay to 200 per cent of cod-liver oil in order to produce the effects which could be produced by a 2-per cent (by rat assay) addition of cod-liver oil. Similar results were reported by Mussehl and Ackerson.[169] In the many subsequent confirmatory observations, which need not be discussed in detail, it was suggested by some that the presence of vitamin A in the cod-liver oil might by a synergistic action account for the greater effectiveness of the natural over the artificial vitamin.[170] This, however, was shown not to be the case by Russell and Klein,[171] and the opinion that the vitamin of cod-liver oil is different from the artificial vitamin was shared by Bills.[172] Thus there appeared to be two forms of the vitamin (but this number has since been increased). Amounts of the two that were equally effective for the rat were not equally effective for the chicken, far less of the natural than of the artificial vitamin being required for that species.[173]

The human seems intermediate between the chick and the rat in its response. Hess, Lewis and Rivkin[174] found that about three rat units of an ergosterol preparation are clinically equivalent to one rat unit of cod-liver oil.[175] Drake,[175a] however, has found no essential difference in their effects on infants.

PRODUCTS RELATED TO CHOLESTEROL AS PRECURSORS OF THE NATURAL D.

Waddell[176] as a result of extensive studies directed toward an explanation of the great effectiveness of direct irradiation of the chick in comparison with the effectiveness of irradiated ergosterol, suggested either that the course of the irradiation changes of ergosterol within the skin is different from that *in vitro* or that the precursor in the skin is not ergosterol. To decide this question, he irradiated crude cholesterol in order to study any products which might be formed in the skin by natural contaminants of cholesterol. It was found that the irradiated crude cholesterol gave better protection against leg weakness in chicks than did irradiated ergosterol, rat unit for rat unit. The idea that this might be ascribed to an improved absorption of ergosterol in the presence of large amounts of cholesterol was excluded by subsequent experiments. When the cholesterol had been purified by refluxing half an hour with hot ethanol containing potassium hydroxide followed by treatment with charcoal, similar good results were obtained. Repeated irradiations of cholesterol with removal of the activated product gradually exhausted the activatability of the cholesterol, indicating that it was not the cholesterol itself which was the provitamin. When ergosterol was irradiated in the presence of purified cholesterol the vitamin produced was no more effective than that resulting from the irradiation of the ergosterol alone. These experiments were important in indicating that there is in crude cholesterol a provitamin other than ergosterol which is capable of yielding a vitamin more potent to chicks than that obtainable from ergosterol.

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[168] Massengale, O. N., and Nussmeier, M., *J. Biol. Chem.*, **87**, 423 (1930).

[169] Mussehl, F. E., and Ackerson, C. W., *Poultry Sci.*, **9**, 334 (1930); *Chem. Abs.*, **26**, 2221 (1932).

[170] See, for example, Dalmer, O., von Werder, F., and Moll, T., *Z. physiol. Chem.*, **224**, 86 (1934).

[171] Russell, W. C., and Klein, D., *Poultry Sci.*, **10**, 269 (1930); *Chem. Abs.*, **26**, 2222 (1932).

[172] Bills, C. E., *Physiol. Rev.*, **15**, 1 (1935). The vitamin from irradiated cholesterol seems as effective as that from cod-liver oil for laying birds. Bethke, R. M., Record, P. R., Wilder, O. H. M., and Kennard, D. C., *Poultry Sci.*, **16**, 438 (1937); *Chem. Abs.*, **32**, 980 (1938).

[173] Other papers relating to these species differences: Russell, W. C., Taylor, M. W., and Wilcox, D. E., *J. Biol. Chem.*, **107**, 736 (1934); Dols, M., *IV Congr. intern. tech. chim. ind. agr. Bruxelles*, **1**, **IC** (1935); *Chem. Abs.*, **30**, 5267 (1936); Supplee, G. C., Flanigan, G. E., Kahlenberg, O. J., and Hess, A. F., *J. Biol. Chem.*, **91**, 773 (1931); Steenbock, H., Kletzien, S., and Halpin, J. G., *Ibid.*, **97**, 249 (1932); Tully, W. C., Hauge, S. M., Carrick, C. W., and Roberts, R. E., *Poultry Sci.*, **10**, 310 (1931); Hunter, J. E., Dutcher, R. A., and Knandel, H. C., *Ibid.*, **11**, 239 (1932); Branion, H. D., and Smith, J. B., *Ibid.*, **11**, 261 (1932); *Chem. Abs.*, **27**, 1032 (1933); King, E. J., Hull, H., and Hall, G. E., *Poultry Sci.*, **12**, 129 (1933); *Chem. Abs.*, **27**, 3504 (1933); DeVaney, G. M., Munsell, H., and Titus, H. W., *Poultry Sci.*, **12**, 215 (1933); *Chem. Abs.*, **27**, 5380 (1933); Halvorson, H. A., and Lachat, L. L., *J. Assoc. Official Agr. Chem.*, **19**, 598, 628, 637, 647 (1936).

[174] Hess, A. F., Lewis, J. M., and Rivkin, H., *J. Am. Med. Assoc.*, **94**, 1885 (1930); Hess, A. F., and Lewis, J. M., *Ibid.*, **99**, 647 (1932); **101**, 181 (1933). *Contra*, Bacharach, A. L., *Food*, **6**, 180 (1937); *Chem. Abs.*, **31**, 5415 (1937).

[175] See also Barnes, D. J., Brady, M. J., and James, E. M., *Am. J. Diseases of Children*, **39**, 45 (1930); Prather, E. O., Nelson, M., and Bliss, A. R., Jr., *Ibid.*, **42**, 52 (1931).

[175a] Drake, T. G. H., *Am. J. Diseases of Children*, **53**, 754 (1937).

[176] Waddell, J., *J. Biol. Chem.*, **105**, 711 (1934).

In crude ergosterol no provitamin other than ergosterol itself could be detected by Bills, Massengale, McDonald and Wirick,[177] in analogous experiments.

Further evidence, now known to have been erroneous, also stimulated the investigation of the non-identity of the vitamin in cod liver oil with that of irradiated ergosterol. Rygh[178] concentrated the vitamin from cod liver oil about 20,000 times and concluded the active product to show no absorption maximum between 2600 and 2700A. Various other properties also differed from those of D_2, which led him to conclude them to be different substances. Ender[179] reached similar conclusions from ultraviolet absorption studies of a concentrate from tuna fish liver oil.

The provitamin of crude cholesterol is destroyed during a purification through the dibromide. The provitamin content of the purified material may then be increased by heat treatment, according to Hathaway and Lobb.[180] This confirmed an earlier observation of Hathaway and Koch[181] who used a temperature of 200°C. At 300°C., however, the provitamin is materially destroyed within four hours. The provitamin was formed in the cholesterol fractions which were the most difficultly soluble in alcohol. There was no evidence of the formation of any ergosterol during the heat treatment and the vitamin produced on irradiation was in its effects on the chick more similar to the natural liver oil vitamin than that obtained by the irradiation of ergosterol. Absorption bands in the heated purified cholesterol were observed by Haman and Steenbock,[182] who also showed that the provitamin is one which yield a vitamin similar to that of the fish oils. They also observed that irradiated plant oils were less effective for chicks than irradiated animal fats, thus aiding in focusing attention upon a derivative of cholesterol as the natural provitamin.

By use of adsorption methods applied to a sample of cholesterol as acetate which contained 4.5 per cent of the new provitamin, Boer, Reerink, Van Wijk and van Niekerk[183] succeeded in isolating the provitamin, first as acetate and after saponification, as the free sterol. It was possible to show its identity with 7-dehydrocholesterol, both by a comparison of the properties of the samples, and by their biological activity after irradiation. By the use of similar chromatographic methods, Brockmann[184] isolated the natural vitamin from tuna fish liver oils and from halibut liver oil.[185]

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[177] Bills, C. E., Massengale, O. N., and Wirick, A. M., *J. Biol. Chem.*, **108**, 323 (1935).

[178] Rygh, O., *Nature*, **136**, 396 (1935).

[179] Ender, F., *Z. Vitaminforschung*, **2**, 241 (1933); **3**, 161 (1934); *Chem. Abs.*, **28**, 4103, 7422 (1934).

[180] Hathaway, M. L., and Lobb, D. E., *J. Biol. Chem.*, **113**, 105 (1936).

[181] Hathaway, M. L., and Koch, F. C., *J. Biol. Chem.*, **108**, 773 (1935).

[182] Haman, R. W., and Steenbock, H., *J. Biol. Chem.*, **114**, 505 (1936); see also Roffo, A. H., Calgano, O., and Roffo, A. E., Jr., *Bull. Soc. Chim. Biol.*, **17**, 203 (1935).

[183] Boer, A. G., Reerink, E. H., van Wijk, A., and van Niekerk, J., *Proc. Acad. Sci. Amsterdam*, **39**, 622 (1936); *Chem. Abs.*, **30**, 5635 (1936).

Windaus, Schenck and van Werder[186] showed that irradiation of 7-dehydrocholesterol in benzene with a magnesium spark gave a product of high antirachitic activity. Tachysterol-3 is first formed. The crude irradiation product was purified through the crystalline dinitrobenzoate and allophanate. These derivatives on saponification yielded the vitamin in the form of a non-crystallizing oil with an absorption maximum at 2650A, similar to that of D_2. The new material was called D_3. It was subsequently obtained in crystalline form by Schenck.[187] It melts at 82-4°C. and has $[\alpha]^{20}_{D} = +83.3°$. It will be noted that 7-dehydrocholesterol has the same disposition of double bonds in the ring B as has ergosterol and the vitamin produced by irradiation differs from D_2 only in the side-chain, the double bond at positions 22 to 23 and the methyl group at carbon 24 of D_2 being lacking in D_3. As first prepared, the rat potency of D_3 appeared somewhat lower than that of D_2, 30×10^6 I.U. per gram as compared with 40×10^6.[188] Subsequently, however, Brockmann and Busse[189] found D_3 crystals from tuna fish liver to have 40,000 I.U. per mg.

Irradiation of 7-dehydrocholesterol with wave-lengths longer than 2800A gives lumisterol-3 which probably differs from lumisterol only in the steric arrangement of groups at carbon atom 10.

The contaminant of cholesterol obtained from spinal cords was found to be 7-dehydrocholesterol or some similar derivative with two double bonds in ring B by Koch and Koch.[190] They believed, however, that the provitamin in heated cholesterol is some quite different material which does not have these double bonds. This material might be present in crude cholesterol, since it was possible to eliminate the impurity with the characteristic absorption spectrum from spinal cord cholesterol and still have a product so potent that, after irradiation, 0.1 to 3.0 mg. equals one rat unit. It was pointed out that the antirachitic potency which can be attained by a provitamin is conditioned not only by the two double bonds in ring B but also by the nature of the side-chain.

The provitamin of pig skin is 7-dehydrocholesterol according to Windaus and Bock,[191] who isolated it as dinitrobenzoate. That of egg yolk sterols is ergosterol.[192] It is possible that there is no ergosterol in skin, since its past identification had been based solely upon the absorption spectrum, which is similar to that of 7-dehydrocholesterol.

An analogous compound, 7-dehydrositosterol, prepared by Wunderlich,[193] was found capable of yielding an antirachitic substance on irradiation, but its potency was forty times less than that of D_2. The dehydrositosterol also undergoes the photosensitized conversion to a pinacol type of bimolecular compound.

[184] Brockmann, H., *Z. physiol. Chem.*, **241**, 104 (1936).

[185] Brockmann, H., *Z. physiol. Chem.*, **245**, 96 (1937). See also Haslewood, G., and Drummond, J. C., *Chemistry and Industry*, 598 (**1936**); Simonds, E., and Zucker, T., *J. Am. Chem. Soc.*, **58**, 2655 (1936); Neracher, O., and Reichstein, T., *Helv. Chim. Acta*, **19**, 1382 (1936). Two or more forms of vitamin may exist in fish oils, according to Bills, C. E., Massengale, O. N., Imboden, M., and Hall, H., *J. Nutrition*, **13**, 435 (1937); Hickman, K. C. D., and Gray, E. LeB., *Ind Eng. Chem.*, **30**, 796 (1938).

[186] Windaus, A., Schenck, F., and von Werder, F., *Z. physiol. Chem.*, **241**, 100 (1936); Windaus, A., Deppe, M., and Wunderlich, W., *Annalen*, **533**, 118 (1937).

[187] Schenck, F., *Naturwiss.*, **25**, 159 (1937). D_3 is said to be twice as active as D_2 on infants by Brockmann, H., *Klin. Wochschr.*, **16**, 1383 (1937).

[188] Zucker, T. F., Simona, E. J., Colman, H. C., and Demarest, B., *Naturwiss.*, **26**, 11 (1938).

[189] Brockmann, H., and Busse, A., *Naturwiss.*, **26**, 122 (1938). See also Ramp, D. G., and Marshall, I. H., *J. Nutrition*, **15**, 525 (1938).

[190] Koch, E. M., and Koch, F. C., *J. Biol. Chem.*, **116**, 757 (1936).

[191] Windaus, A., and Bock, F., *Z. physiol. Chem.*, **245**, 168 (1936).

[192] Windaus, A., and Stange, O., *Z. physiol Chem.*, **244**, 218 (1936).

[193] Wunderlich, W., *Z. physiol. Chem.*, **241**, 116 (1936).

Urushibara and Ando[194] described the photochemical dehydrogenation of an alcoholic solution of 7-dehydrocholesterol by sunlight in the presence of eosin. After a week there were obtained flocculent needles considered to be, in analogy with the behavior of ergosterol, 7-dehydrocholestenopinacone.

A search has been made for other provitamins. Weinhouse and Kharash[195] irradiated a series of tertiary alcohols or their dehydration products obtained by the action of various Grignard reagents on 7-ketocholesteryl acetate. The only one which showed slight antirachitic activity when irradiated was 7-isobutylidenecholesterol. Uraki[196] observed that irradiation of α-cholatrienic acid in chloroform for nine hours changed the specific rotation from −22.63° to +2.4°. The product was a non-crystallizing resin which could be hydrogenated to cholanic acid. The β-choladienic acid from desoxycholic acid was not altered by ultraviolet rays. It appeared that the point of attack in cholatrienic acid was the B ring, a shifting of the double bond occurring. Kikuzawa[197] reported the irradiated methyl α-cholate to have a slight antirachitic action. The β- derivative had less.

Rygh[198] recently found evidence for the occurrence in butter and ether extracts of hay and beef liver of an antirachitic substance which differed from other antitrachitic vitamins in occurring to a larger extent in the saponifiable than in the unsaponifiable fraction. Kon and Booth[199] observed that the saponification of butter caused a loss of 80 per cent of its antirachitic potency.

The sterols from cacao-bean butter (theosterols) can be made antirachitic by irradiation.[200]

A recent review of the relative potencies for the rat and the chick of the antirachitic substances produced, chemically, by irradiation, or occuring in natural sources (particularly the fish liver oils of different species), has been given by Bills.[201] Grab[202] concluded the crystalline product from irradiated 7-dehydrocholesterol to be equivalent in its effects on the rat and the chick to a crystalline product isolated from tuna-liver oil. This material he called D_3. The difference of a methyl group between irradiated 7-dehydrocholesterol and irradiated 22-dihydroergosterol resulted in but little difference in physiological activity. Sterols with 29 carbon atoms are scarcely to be considered natural provitamins since the activities of 7-dehydrositosterol and 7-dehydrostigmasterol were very low. D_2 is somewhat less potent on the rat and considerably less potent on the chick than D_3.

Colorimetric methods are of limited use for the assay of vitamin D_2. These are based upon the spectrophotometric measurement of the intensity of an absorption band at 5000A produced by the addition of antimony trichloride or of one produced by aluminum chloride.[203] A color test with sodium selenite is given by D_2 but not by cholesterol before or after irradiation.[204] Biological assay methods, however, have been employed most frequently in the development of our knowledge of these substances. Their discussion, as well as that of the effects of the sterol irradiation products on the mineral metabolism, lies beyond the scope of this work.

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[194] Urushibara, Y., and Ando, T., *Bull. Chem. Soc. Japan*, **11**, 802 (1936); **12**, 495 (1937); *Chem. Abs.*, **31**, 2100 (1937). For similar work on 2,4-cholestadiene, see Skau, E. L., and Bergmann, W., *J. Am. Chem. Soc.*, **60**, 986 (1938); Butenandt, A., and Kudssus, H., *Z. physiol. Chem.*, **253**, 1, 224 (1938).

[195] Weinhouse, S., and Kharash, M. S., *J. Org. Chem.*, **1**, 490 (1936).

[196] Uraki, J., *Z. physiol. Chem.*, **221**, 40 (1933); *Chem. Abs.*, **28**, 168 (1934).

[197] Kikuzawa, T., *Z physiol. Chem.*, **220**, 54 (1933); see also Okii, I., *J. Biochem. Japan*, **18**, 45 (1933); *Chem. Abs.*, **27**, 5425 (1933).

[198] Rygh, O., *Nature*, **133**, 533 (1934); *Z. Vitaminforschung*, **3**, 164 (1934); *Chem. Abs.*, **28**, 7315 (1934).

[199] Kon, S. K., and Booth, R. G., *Biochem. J.*, **27**, 1302 (1933); **28**, 111 (1934).

[200] Labbe, H., de Balsac, F., and Lerat, R., *Bull. soc. therap.*, **35**, 71 (1930); *Chem. Abs.*, **24**, 982 (1930); **25**, 729 (1931); Knapp, A. W., and Coward, K. H., *Biochem. J.*, **29**, 2728, (1935).

[201] Bills, C. E., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 328 (1935); *J. Am. Med. Assoc.*, **108**, 13 (1937). *Cf.* also Hume, E. M., *Nutrition Abstracts and Reviews*, **6**, 891 (1937); von Wendt, G., *Voprosy Pitaniya*, **5**, No. 4, 31 (1936); *Chem. Abs.*, **31**, 2659 (1937).

[202] Grab, W., *Z. physiol. Chem.*, **243**, 63 (1936).

[203] Brockmann, H., and Chen, Y. H., *Z. physiol. Chem.*, **241**, 129 (1936); Emmerie, A., and van Eekelen, M., *Acta Brevia, Neerland. Physiol., Pharmakol. Microbiol.*, **6**, No. 9-10, 133 (1936); *Chem. Abs.*, **31**, 1448 (1937); Halden, W., and Tzoni, H., *Nature*, **137**, 909 (1936); *Naturwiss.*, **24**, 296 (1936); Tzoni, H., *Biochem. Z.*, **287**, 18 (1936); Brückner, J., *Biochem. Z.*, **270**, 346 (1934); Wait, R., *Pharm. Zentralhalle*, **78**, 237 (1937).

Physiological Effects. In general, the administration of pure irradiation products leads to the effects on blood calcium and phosphorus and on bone calcification that result on general irradiation of the experimental animal. It would add but little to recount the many earlier experiments in which indefinite irradiation products, frequently contaminated with either inert or with predominantly toxic products, had been used.[205]

Robinson and Rosenheim[206] found vitamin D to exert no demonstrable action on the calcification or decalcification of bone slices *in vitro*, but Venar and Todd[207] report that the extent and density of mineralization of bone fragments from rachitic mice may be increased by the addition of small amounts of an aqueous emulsion of irradiated ergosterol to the calcifying medium in which the bones are immersed. Similar effects may be attained by the use of cod-liver oil or by irradiating the cultures by a sunlamp.[208]

Harris[209] believes the vitamin to function by increasing the net absorption of calcium and phosphates from the intestine, thus tending to raise the level of the blood calcium or phosphate. The latter rise automatically brings about increased calcification in sites provided with the bone-calcifying enzyme, phosphatase. Hottinger[210] suggested that it renders innocuous some inhibitor of calcium assimilation, possibly an enzyme capable of decomposing glycerophosphates or hexosephosphates. Taylor and Weld[211] were of the opinion that, at least in young dogs, there is no evidence that irradiated ergosterol increases calcium absorption; indeed they state that even small doses increase the excretion of calcium.

One speculation as to the mechanism by which the vitamin functions regards it as liberating inorganic phosphorus from the lipins of the body, a deficiency of inorganic phosphate being regarded as the essential cause of rickets.[212] Nicolaysen[213] finds that in rachitic rats, inorganic phosphorus is reduced in the muscles, liver and kidneys. Massive doses of the vitamin increased it to normal, but therapeutic doses caused only a slight increase of the inorganic phosphorus of the kidney.[214] In D deficient rats, the percentage of inorganic phosphorus in the red blood cells is reduced, but that of easily hydrolyzable phosphoric esters is increased.[215] Warkany[216] observed that rabbits which usually excrete no phosphates, eliminate large quantities in the urine within 48 hours after the administration of 30 to 100 mg. of irradiated ergosterol in their food.

In artificial cultures of the skeletal tissues of the embryo chick, phosphatase appears early.[217] Heymann[218] found that under the influence of irradiated ergosterol, phosphatase activity *in vitro* is unchanged, but ultraviolet irradiation caused inhibition of the enzyme in about 40 per cent of the tests. The enzyme is greatly increased in chicks with rickets.[219] In laying hens there is a high range of variation of the serum phosphatase which is not reduced by the administration of irradiated ergosterol. Plasma phosphatase is increased in rachitic children less than two years of age. Its continued rise may be prevented by the use of vitamin D.[220]

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[204] Levine, V. E., and McKay, F. M., *Proc. Soc. Exp. Biol. Med.*, **33**, 546 (1936).

[205] See Laurens, H., "The Physiological Effects of Radiations." New York, The Chemical Catalog Co., Inc., (Reinhold Publishing Corp.) 1933. For more recent studies, Crimm, P. D., Strayer, J W., Watson, H. L., and Heimann, G., *Am. Rev. Tuberc.*, **28**, 202 (1933); *Chem. Abs.*, **28**, 806 (1934); Morgan, A. F., Garrison, E. A., Householder, H., Hansen, A M., Seberger, M. V., Watenpaugh, J. T., Felsher, A., and Long, N. L., *Univ. California Pub. Physiol.*, **8**, 61 (1934); *Chem. Abs*, **28**, 7315 (1934); Freeman, S., *Am. J. Physiol.*, **115**, 701 (1936); Johnson, R. M., *J. Clin. Investigation*, **16**, 223 (1937).

[206] Robison, R , and Rosenheim, A. H., *Biochem. J.*, **28**, 684 (1934).

[207] Venar, Y., and Todd, T. W., *J Lab Clin. Med.*, **22**, 221 (1936); see also Dejust, L. H , *Rev. actinologie physiotherap.*, **6**, 1 (1931); *Chem. Abs.*, **26**, 2792 (1932).

[208] Yoshitomi, M., *J. Biochem. Japan*, **21**, 37 (1935); *Chem. Abs.*, **29**, 2590 (1935).

[209] Harris, L., *Lancet*, **I**, 1031 (1932); *Chem. Abs* , **27**, 2187 (1933).

[210] Hottinger, A., *Naturwiss.*, **16**, 484 (1928).

[211] Taylor, N. B., and Weld, C. B., *Trans. Roy. Soc. Canada*, **26**, 9 (1932); *Chem. Abs.*, **27**, 1922 (1933).

[212] McGowan, J. P., Cunningham, I. J., and Auchinachie, D. W., *Biochem. J.*, **25**, 1295 (1931); McGowan, J. P., *Ibid.*, **27**, 943 (1933).

[213] Nicolaysen, R., *Biochem J.*, **30**, 1329 (1936); *see also Biochem. J.*, **31**, 101, 105, 107, 122, 328 (1937).

[214] See also Jones, J. H., and Cohn, B. N. E., *J. Nutrition*, **11**, 293 (1936); Duffau, R., [*Compt rend soc. biol.*, **124**, 1194 (1937)] finds an increase of about 10% in the orthophosphates of muscles in rickets.

[215] Von Euler, H., and Brandt, K., *Z. physiol. Chem.*, **240**, 215 (1936).

[216] Warkany, J., *Klin. Wochschr.*, **9**, 2152 (1930); *Chem. Abs.*, **25**, 1877 (1931).

Morelle[221] studied the healing of experimental fractures in three groups of rats receiving respectively 1, 10, and 2 to 4 mg. of irradiated ergosterol per day. No effects were apparent before the twentieth day, but after that time the fracture lines were invisible in those receiving the medium dose, although they were still apparent in controls. After the thirtieth day, there was a dense callus in the treated animals and in the controls the disappearance of the fracture line had just begun. Heavy doses caused abnormally dense and exuberant callus formation. The conclusion of Grauer[222] from similar experiments was that therapeutic doses stimulate the osteogenic layer and favor repair. Overdoses stimulate the fibrous layer of the periosteum by decalcification of bones and retard repair. Fischer and Key,[223] however, are of the opinion that the addition of either calcium or vitamin D to the diet does not lessen the local atrophy of disuse or accelerate the union of bones.

Although some have expressed the view that the vitamin acts by stimulating the parathyroids, this is by no means generally conceded.[224] Comel[225] believed that after removal of the parathyroids life could be maintained indefinitely by giving vitamin D, but Lesné, Dubois and Simonnet[226] find that it does not serve as a substitute for the hormone.[227]

Dosage. As early as 1927, reports of the clinical efficacy of irradiated ergosterol began to appear.[228] The use of a preparation of irradiated ergosterol as a comparison standard for the assay of the antirachitic action was described by Coward and adopted by the British Pharmaceutical Society.[229] Its potency was such that a daily dose of not more than 0.1γ produced complete healing of rickets induced in rats under prescribed conditions. The unit of antirachitic potency was then defined as the amount of activity contained in 0.1γ of the standard preparation. The standard subsequently adopted by the Medical Research Council was prepared by freeing the irradiation product from alcohol, and dissolving it in pure unadulterated olive oil, the volume being adjusted to make a known concentra-

[217] Croxatio, H., *Compt. rend. soc. biol.*, **108**, 117 (1931); *Chem. Abs.*, **26**, 3009 (1932); see also Fischmann, C. F., *Arch. exptl. Zellforsch.*, **19**, 211 (1937); *Chem. Abs.*, **31**, 8618 (1937).

[218] Heymann, W., *Biochem. Z.*, **227**, 1 (1930); see also Bauer, W., Marble, A., and Claflin, D., *J. Clin. Investigation*, **11**, 21, 37, 47 (1932).

[219] Common, R. H., *J. Agr. Sci.*, **26**, 492 (1936); *Chem. Abs.*, **30**, 8327 (1936).

[220] Stearns, G., and Warweg, E., *Am. J. Diseases of Children*, **49**, 79 (1935); *Chem. Abs.*, **29**, 2581 (1935); Morris, N., Stevenson, M. M., Peden, O. D., and Small, J., *Arch. Diseases of Childhood*, **12**, 45 (1937). Compare earlier negative findings of Fabisch, W., *Biochem. Z.*, **254**, 158 (1932); *Chem. Abs.*, **27**, 525 (1933) and Rossi, A., and De Rienzo, A., *Boll. soc. ital. biol. sper.*, **8**, 719 (1933); *Chem. Abs.*, **29**, 2557 (1935).

[221] Morelle, J., *Rev. Belge Sci.*, **2**, 226 (1930); *Chem. Abs.*, **25**, 2463 (1931).

[222] Grauer, R. C., *Arch. Surgery*, **25**, 1035 (1932); *Chem Abs.*, **27**, 1946 (1933).

[223] Fischer, F., and Key, J. A., *Archiv. Surgery*, **29**, 3112 (1934); *Chem. Abs.*, **28**, 6796 (1934).

[224] Thomson, D. L., and Collip, J. B., *Physiol. Rev.*, **12**, 309 (1932).

[225] Comel, M., *Arch. Fisiol.*, **29**, 123 (1930); *Chem. Abs.*, **26**, 180 (1932).

[226] Lesné, E., Dubois, R., and Simonnet, H., *J. Physiol. Path. Gén.*, **30**, 65 (1932); *Chem. Abs.*, **26**, 4876 (1932).

[227] See also Popoviciu, G., and Nitzescu, I. I., *Z. ges. Exptl. Med.*, **81**, 656 (1932); *Chem. Abs.*, **27**, 4565 (1933); Asher, D. W., and Jones, J. H., *J. Biol. Chem.*, **100**, 333 (1933); Stacey, R. S., *Lancet*, **II**, 656 (1935); Deutsch, H., Reed, C. I., and Struck, H. C., *Am. J. Physiol.*, **117**, 1 (1936); Brougher, J. C., *Ibid.*, **86**, 538 (1928); Morgan, A. F., and Garrison, E. A., *J. Biol. Chem.*, **85**, 687 (1930); Mathieu, F., *Compt. rend. soc. biol.*, **114**, 1375 (1933); *Chem. Abs.*, **28**, 1744 (1933); Dale, H. H., Marble, A., and Marks, H. P., *Proc. Roy. Soc.*, **111B**, 522 (1932).

[228] Hess, A. F., *J. Am. Med. Assoc.*, **89**, 337 (1927); Schippers, J. C., *Nederland. Tijdschr. Geneesk.*, **72**, 3898 (1928); *Chem. Abs.*, **22**, 4154 (1928); Sobel, J., and Claman, I., *Arch. Ped.*, **46**, 1 (1929); *Chem. Abs.*, **23**, 1938 (1929).

[229] Coward, K. H., *Quart. J. Pharm.*, **1**, 27 (1928); *Chem. Abs.*, **22**, 4154 (1928); *Lancet*, **II**, 503 (1930).

tion in terms of the ergosterol used. Such solutions retained their activity unchanged for two years if maintained at or below 0°C.

In practice, cod-liver oil was checked against this standard and adjusted to contain a definite concentration of the vitamin in terms of the standard. Unfortunately, much confusion arose in regard to the strength of the cod-liver oil adopted as comparison standard. The system of the British Medical Research Council called for a cod-liver oil containing 100 units per cc. This was altered by the League of Nations to 100 units per gram, the strength adopted in the U. S. Pharmacopoeia in 1934. The Steenbock system used an oil standardized to contain 37 units per gram and the Holmes system (employed for a time by the American Drug Manufacturers Association) one with 350 units per gram. Still other systems have been used in other countries.[230]

The present vitamin D unit[231] is equivalent to 0.025γ of calciferol.

Bills[232] considers that the smallest dose which can be relied on to prevent rickets or to heal mild rickets in infants is about 3000 international units (I.U.) per day in the form of irradiated ergosterol or 1000 I.U. in the form of cod-liver oil. The Council on Pharmacy and Chemistry of the American Medical Association[233] adopted the name Viosterol to designate irradiated ergosterol and Viosterol in Oil to designate a preparation containing the substance dissolved in oil. The qualifying phrases 100 D, 5 D, etc. were added to the label to indicate the potency as a multiple of the potency of good cod-liver oil.

The successful use of large doses, 10 to 20 drops daily of viosterol, in late rickets was described by Shelling and Hopper.[234] Spence[235] found calciferol as effective as cod-liver oil or irradiated ergosterol in human rickets. One cc. of a solution containing 3000 units, administered daily, produced a maximum curative effect.

Recently, there has been much discussion as to the effects of variations in the calcium and phosphorus of the diet given during the administration of the vitamin, but this cannot be considered here.[236]

Toxic Effects. Hypervitaminosis D. About 1928, it became evident that irradiated ergosterol preparations may exert toxic effects.[237] Particularly dangerous properties were ascribed to the imported Vigantol.[238] After the administration of large quantities of this material to rats, Herzenberg[239] observed a necrosis in the smooth and striated muscles, followed by a deposition of calcium in the necrotic areas. The deposition of calcium was observed in the heart muscle and in elastic muscle fibers of blood vessel walls but the changes were different in character from those of arteriosclerosis. Schoenholz[240] found that pregnant rats which had received an overdose (10 mg. of Vigantol per day), lost their appetities and became sick. The fetuses were resorbed *in utero* or aborted. The live young were very small and usually died. Calcium deposits were observed in the livers of some of the mothers. A number of German workers observed involvement of the kidneys. These observations stimulated a great number of publications, of which but a few need be cited.[241]

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[230] See Bills, C. E., *Physiol. Rev.*, **15**, 1 (1935).

[231] *Quart. Bull. Health Org. League of Nations*, **3**, 428 (1934).

[232] Bills, C. E., *Physiol. Rev.*, **15**, 1 (1935).

[233] *J. Am. Med. Assoc.*, **93**, 693 (1929).

[234] Shelling, D. H., and Hopper, K. B., *Am. J. Diseases of Children*, **47**, 61 (1934).

[235] Spence, J. C., *Lancet*, **225**, 911 (1933); *Chem. Abs.*, **28**, 5503 (1934).

[236] See Bruce, H. M., and Callow, R. K., *Biochem. J.*, **28**, 512 (1934).

[237] Wurzinger, S., *Klin. Wochschr.*, **7**, 1859 (1928); *Chem. Abs.*, **24**, 3042 (1930); Reyher, P., and Walkoff, E., *Münch. Med. Wochschr*, **75**, 1071 (1928); *Chem. Abs.*, **23**, 4728 (1929); Kreitmair, H., *Münch. Med. Wochschr.*, **75**, 637 (1928); Lasch, F., *Klin. Wochschr.*, **7**, 2148 (1928).

[238] Hess, A. F., and Lewis, J. M., *J. Am. Med. Assoc.*, **91**, 783 (1928).

[239] Herzenberg, H., *Beitr. Path. Anat.*, **82**, 27 (1929); *Chem. Abs.*, **23**, 4725 (1929); (Sclerosis in Man), Gerlach, W., *Münch. Med. Wochschr.*, **83**, 49 (1936).

[240] Schoenholz, L., *Klin. Wochschr.*, **8**, 1257 (1929); *Chem. Abs.*, **24**, 890 (1930).

A toxic calcification factor was defined[242] as the smallest amount which, given daily for a period of ten days, causes a mouse to lose 2.5 gm. in weight or to die. Mice receiving larger doses showed calcareous deposits in the kidneys. The ratio between the antirachitic rat dose and the mouse calcification factor was considered the therapeutic index of an irradiated ergosterol preparation.

It soon became evident that there were considerable differences between the antirachitic and toxic doses of variously irradiated preparations. With Vigantol, the margin of safety was very narrow.[243] The spectrographic study of the irradiation process soon made it apparent why this was the case. It was prepared according to a patent[244] which directed that the irradiation be continued until spectrographic observations indicated that there had been a maximum formation of a substance absorbing chiefly at 2480A. This is, as has been stated in a preceding section, now known to be toxisterol or substance 248, the overirradiation product. Subsequently it has been learned that D_2 and even the D_3 of cod-liver oil are also toxic in large doses. It is, however, evident that the formation of substance 248 should be avoided, since it is not only toxic but its formation occurs at the expense of that of the true antirachitic substance. The toxicity of calciferol in large doses was demonstrated by Askew, Bourdillon, Bruce, Callow, Philpot and Webster and by other research groups.[245]

At one time, Holtz and Schreiber[246] believed that the true vitamin when isolated would prove nontoxic and attempts were made to employ partition between immiscible solvents and various chemical procedures for separating the assumed toxic and antirachitic fractions. The failure of these attempts and the observation that D_1 had toxic properties led Windaus, Busse and Weidlich[247] to agree that the true vitamin possesses toxicity. It was found possible by chemical means to destroy the antirachitic activity without lessening the toxicity, but the converse was not possible. The English workers found that the ratio of the toxic dose in mice to the curative dose in rats is about 4000 to 1. The finding that D_2 has toxic properties proved[248] that Reiter had been in error in claiming that irradiation with wave-lengths longer than 2800A produces a non-toxic product.[249] It is, of course, true that the use of such long wave-lengths lessens the danger of the production of the toxic substance 248 by overirradiation. Whether or not tachysterol itself has toxic properties is not yet known, but its thermal decomposition products are highly toxic.[250]

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[241] Bamberger and Spranger, *Deut. Med. Wochschr*, **54,** 1116 (1928); Wiskott, A., *Munch. Med. Wochschr.*, **75,** 1445 (1928), Adam, A., *Klin. Wochschr.*, **7,** 1825 (1928); Degkwitz, R., *Münch. Med. Wochschr.*, **75,** 1631 (1928); Bamberger, Ph., *Deut. Med. Wochschr.*, **55,** 399 (1929); György, P., *Klin. Wochschr.*, **8,** 684 (1929); Putschar, W., *Z. Kinderheilk.*, **48,** 269 (1929); Klausner-Cronheim, I., *Deut. Med. Wochschr.*, **56,** 1566 (1930).

[242] Holtz, F., Lacquer, F., Kreitmair, H, and Moll, T., *Biochem. Z.*, **237,** 247 (1931); *Münch. Med. Wochschr.*, **78,** 1688 (1931); *Chem. Abs.*, **26,** 3011 (1932).

[243] Göttche, O., and Kellner, B., *Arch. Kinderheilk.*, **94,** 129 (1931).

[244] British P. 296,093, Nov. 15, 1928, to I. G. Farbenind. A.-G.

[245] Askew, F. A., Bourdillon, R. B., Bruce, H. M., Callow, R. K. Philpot, J., and Webster, T. A., *Proc. Roy. Soc.*, **109,** 488 (1932); Dale, H H., Marble, A., and Marks, H. P., *Ibid.*, **111B,** 522 (1932); Gough, J, Duguid, J. B., and Davies, D. R, *Brit J. Exptl. Path.*, **14,** 137 (1933); Harris, L. J, and Moore, T., *Biochem. J.*, **22,** 1461 (1928); Harris, L. J., and Innes, J., *Ibid.*, **25,** 367 (1931).

[246] Holtz, F., and Schreiber, E., *Z physiol Chem.*, **191,** 3 (1930), Windaus, A., and Auhagen, E., *Z. physiol. Chem.*, **196,** 108 (1930); **197,** 167 (1931).

[247] Windaus, A., Busse, P., and Weidlich, G., *Z. physiol. Chem.*, **202,** 246 (1931).

[248] Laquer, F., *Klin. Woch.*, **10,** 1072 (1931); *Deut. Med. Wochschr.*, **57,** 243 (1931); *Chem. Abs.*, **26,** 3010 (1932).

[249] Reiter, T., *Naturwiss.*, **17,** 876 (1929); Kisch, E., and Reiter, T., *Deut. med. Wochschr.*, **56,** 2034 (1930); *Chem. Abs.*, **25,** 4918 (1931).

[250] Windaus, A., and Lüttringhaus, A., *Deut. Med. Wochschr.*, **58,** 1669 (1932).

A review of the nature of the toxic effects of D_2 and of cod-liver oil has been given by Agduhr, Blix and Vahlquist.[251] A fatal case in a child has been described by Thatcher.[252] Ham and Lewis [253] found that large doses of vitamin D given to normal young rats interfered with the processes of bone calcification and actually produced rachitic lesions. They suggested that the action may be to increase the attraction of the blood for calcium. Baumgartner, King and Page [254] found overdoses to produce softening of the skeletal framework of rabbits and a low bone phosphatase. The ratio of calcium to phosphorus in the bone is not affected according to Kramer, Shear and McKenzie.[255]

That the hypercalcemia alone is not responsible for the toxic effects, since it is compatible with life, is the belief of Taylor, Weld and Sykes.[256]

It is generally found that the hypercalcemia may be produced even on a low calcium diet, some claiming at the expense of the bones.[257]

Daily subcutaneous injections of irradiated ergosterol produce local calcification in the subcutaneous tissues, according to von Brand and Holtz. Calcification in the kidneys is less than after the oral administration of the same doses.[258] In general, after a toxic state with calcium deposition has been reached, the discontinuance of the administration of the vitamin leads to a reversal of the process and the repair of the lesions.[259] Both human subjects and dogs usually survive 20,000 to 30,000 units per kg. per day for indefinite periods. In rats, it is agreed by many that 10,000 times the minimum antirachitic dose is not lethal and several say not harmful.[260] Bills and Wirick [261] found 1000 times overdosage to be just perceptibly harmful, 4000 times overdosage to be definitely injurious and 40,000 times overdosage strongly toxic. Harris and Moore [262] found a 100,000 times overdosage rapidly fatal, and Collazo, Rubino and Varela Fuentes [263] found 50,000 times the normal dose fatal within six weeks. Young rats and puppies remained normal with doses up to 1000 times the minimal effective dose according to Cartland, Speer and Heyl.[264]

[251] Agduhr, E., Blix, G., and Vahlquist, B., *Uppsala Läkareforeningen*, **39**, 304; **40**, 183; *Chem. Abs.*, **29**, 8145 (1935); for the pathologic anatomy, Duguid, J. B., *Lancet*, **II**, 983 (1930); Barr, D P., *Physiol. Rev.*, **12**, 593 (1932); Nitzescu, I. I., and Bratiano, S., *Compt. rend. soc. biol.*, **121**, 1533 (1936).

[252] Thatcher, L., *Edinburgh Med. J.*, **38**, 457 (1931); *Chem. Abs.*, **25**, 5446 (1931).

[253] Ham, A. W., and Lewis, M. D., *Brit. J. Exptl Path.*, **15**, 228 (1934); *Chem. Abs.*, **28**, 7301 (1934).

[254] Baumgartner, L., King, E. J, and Page, I. H., *Biochem. Z.*, **213**, 170 (1929); *Chem. Abs.*, **24**, 403 (1930).

[255] Kramer, B., Shear, M., and McKenzie, M. R., *J. Biol. Chem.*, **82**, 555 (1929).

[256] Taylor, N. B., Weld, C. B., and Sykes, J. F., *Brit. J. Exptl. Path.*, **17**, 104 (1936). For the effects of small doses of concentrated preparations on the blood calcium and phosphorus of monkeys, see Cowdry, E. V., and Scott, G. H., *Arch. Path.*, **22**, 1 (1936).

[257] Soeur, R., *Arch. Int. Med. Exptl.*, **6**, 365 (1931); *Chem. Abs.*, **25**, 4588 (1931); Jones, J. H., and Rapoport, M., *J. Biol. Chem.*, **93**, 153 (1931); Jones, J. H., and Robson, G. M., *Ibid.*, **91**, 43 (1931); Thoenes, F., *Jahrbuch Kinderheilk.*, **126**, 348 (1929); *Chem. Abs.*, **26**, 501 (1932); *Jahrb. Kinderheilk.*, **129**, 171 (1930); Jones, J. H., Rapoport, M., and Hodes, H. L., *J. Biol. Chem.*, **89**, 647 (1930); Wiskott, A., *Z. Kinderheilk.*, **49**, 79 (1930); *Chem. Abs.*, **26**, 4362 (1932); Kern, R., Montgomery, M. E., and Still, E. U., *J. Biol. Chem.*, **93**, 365 (1931); Cole, V. V., and Koch, F. C., *Ibid.*, **94**, 263 (1931); Hess, A. F., Benjamin, H., and Gross, J., *Ibid.*, **94**, 1 (1931); Pozzi, L., and Preto, E., *Biochem. terap. sper.*, **18**, 397 (1932); *Chem. Abs.*, **27**, 1667 (1933); Kletzien, S. W. F., Templin, V. M., Steenbock, H., and Thomas, B. H., *J. Biol. Chem.*, **97**, 265 (1932); von Euler, H., and Rydbom, M, *Biochem. Z.*, **249**, 141 (1932); Popoviciu, G., *Jahrb. Kinderheilk.*, **132**, 286 (1931); *Chem. Abs.*, **26**, 3013 (1932).

[258] von Brand, T., and Holtz, F., *Z. physiol. Chem.*, **195**, 241 (1931).

[259] Steck, I. E., Deutsch, H., Reed, C. I., and Struck, H. D., *Ann. Internal Med*, **10**, 951 (1937); von Brand, T., and Holtz, F., *Z. physiol. Chem.*, **185**, 217 (1929); for storage after massive doses, see Heymann, W., *J. Biol. Chem.*, **118**, 371 (1937).

[260] Rosenheim, O., and Webster, T. A., *Biochem. J.*, **21**, 389 (1927); Light, R. F., Miller, G. E., and Frey, C. N., *J. Biol. Chem.*, **84**, 487 (1929).

[261] Bills, C. E., and Wirick, A. M., *J. Biol. Chem.*, **86**, 117 (1930).

[262] Harris, L. J., and Moore, T., *Biochem. J.*, **22**, 1461 (1928).

[263] Collazo, J. A., Rubino, P., and Varela Fuentes, B., *Biochem. Z.*, **204**, 347 (1929).

[264] Cartland, G. F., Speer, J. H., and Heyl, F. W., *J. Pharmacol.*, **36**, 619 (1929); *Chem. Abs.*, **24**, 404 (1930).

In the human, no ill effects were noted with 20 to 50 times the ordinary doses by Hess, Poncher, Dale and Klein,[265] other than a tendency to constipation and colic. In patients with tetany no toxic effects were noted with 300 times overdosage.[266] Bills believes that in man toxic effects begin to appear at 200 times the ordinary dose, that is when 600,000 I.U. of properly irradiated ergosterol are given daily over several weeks. Rappaport and Reed gave 3 cc. per day of a concentrated solution 10,000 D, and known to contain a million I.U. per gram. Although this was 2,760,000 I.U. or 920 times the ordinary therapeutic dose, no serious poisoning was produced. The largest recorded human dose, 6000 times the ordinary dose, produced hypercalcemia, but no pathological calcification of tissues.[267]

Excessive doses of fish-liver oils are less apt to produce hypervitaminosis.[268]

Relation to Tuberculosis. Because of the remedial effects of ultraviolet irradiation of tuberculous patients, many studies have been made of the effects of vitamin D in that disease in order to determine whether its action may account for the effects of general irradiation. The calcifying action of the vitamin might be expected to be of value in the treatment of the disease.[269] Simonnet and Tanret[270] found large doses of irradiated ergosterol to cause a notable increase in pulmonary calcification in tuberculous rabbits. In chronic tuberculosis the evolution of tubercles was checked. Pfannstiel and Scharlau[271] reported somewhat less favorable results on rabbits primarily infected but found favorable results in somewhat immunized rabbits. Meersseman and Tricault[272] found tuberculous guinea pigs given vitamin D to live longer and have less severe lesions than the controls. They also reported improvement in eleven human patients. Spies and Berryhill[273] sugested a diet high in vitamin D for patients with intraperitoneal tuberculosis. Long[274] agreed that viosterol by mouth increases calcification in experimental tuberculosis.

Many of those who obtained negative results did not employ massive doses.[275] Haubold[276] even claimed that small doses stimulated the disease in guinea pigs. Spies and Walker[277] obtained less distinct results in experimental avian than in the bovine tuberculosis. Poncher and Gasul[278] drew no conclusions as to the effect of moderately large doses in tuberculous children, but believed the secondary effects of such therapy unfavorable. Negative results in intestinal tuberculosis have been reported by Steinbach and Rosenblatt.[279] More or less favorable evidence for the use of irradiated ergosterol in tuberculosis is also to be found in the following papers.[280]

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[265] Hess, J. H., Poncher, H. G., Dale, M. L., and Klein, R. I., *J. Am Med. Assoc.*, **95**, 316 (1930).

[266] Reed, C. I., and Seed, L., *Endocrinology*, **17**, 136 (1933); but see Rappaport, B. Z., and Reed, C. I., *J. Am. Med. Assoc*, **101**, 105 (1933).

[267] Spies, T. D., and Hanzal, R. F., *Proc. Soc Exptl. Biol. Med.*, **31**, 747 (1935).

[268] Morgan, A F., Kimmel, L., and Hawkins, N. C, *J. Biol. Chem*, **120**, 85 (1937); Martinelli, A., *Probl. alimentare*, **4**, 1 (1934); *Ber. ges. Physiol. exptl. Pharmakol.*, **87**, 82; *Chem. Abs.*, **31**, 7951 (1937).

[269] The subject has been reviewed by Guilbert, G. D., *Med. Bull. Veterans' Admin.*, **10**, 141 (1934). See also Kaminsky, J., and Davidson, D., *Am. Rev. Tuberc.*, **22**, 48 (1930); Hildebrand, C. J., *Ibid.* **22**, 53 (1930).

[270] Simonnet, H, and Tanret, G, *Compt rend.*, **190**, 1526 (1930).

[271] Pfannstiel, W., and Scharlau, B., *Beitr. klin. Tuberk.*, **73**, 351 (1930); *Chem Abs.*, **25**, 2172 (1931).

[272] Meersseman, F., and Tricault, G., *Semana Med. Buenos Aires*, **I**, 595 (1931); *Chem. Abs.*, **25**, 2485 (1931).

[273] Spies, T., and Berryhill, W. R., *Am. Rev. Tuberc.* **26**, 275 (1932); *Chem. Abs*, **27**, 775 (1933).

[274] Long, E. R., *Proc. Soc. Exptl. Biol. Med*, **30**, 1090 (1933).

[275] Simonnet, H, and Tanret, G., *Presse Med.*, **39**, 932 (1931); Grayzel, H. G., Shear, M. J., and Kramer, B., *Am. Rev. Tuberc.*, **24**, 106 (1931); Kaminsky, J., and Davidson, D. L., *Ibid.*, **24**, 483 (1931); Freund, R., *Beitr. klin. Tuberk.*, **78**, 666 (1931); *Chem. Abs.*, **26**, 6012 (1932); Zeyland, J., and Piasecka-Zeyland, E., *Tubercle*, **17**, 198 (1936); Crimm, P. D., and Strayer, J. W. *Ann. Int. Med.*, **9**, 1393 (1936); Loewen, D. F., and Oatway, W. H., *J. Am. Rev. Tuber*, **33**, 733 (1936).

[276] Haubold, H., *Z. Tuberk.*, **67**, 247 (1933); *Chem. Abs.*, **27**, 5100 (1933).

[277] Spies, T., and Walker, T. T., *Am. Rev. Tuberc.*, **64**, 23, 65 (1931); **74**, 723 (1931).

[278] Poncher, H. G, and Gasul, B M., *Am. Rev. Tuberc.*, **30**, 358 (1934); *Chem. Abs.*, **28**, 7303 (1934).

DeJust[281] reported the cure of two cases of tuberculous osteitis with fistulas after a score of instillations of viosterol into the fistulas.

Other Effects. Mellanby[282] called attention to the fact that exposure of puppies on a moderately defective diet to the rays of a mercury arc had a beneficial effect upon the calcification and structure of the teeth. If the diets were very bad, however, the calcification became poorer on irradiation. Later, Mellanby and Pattison[283] found a cereal-free diet rich in calcium and vitamin D to almost eliminate the initiation and spread of caries in children. Similar favorable reports are due to Agnew, Agnew and Tisdall[284] and others.[285] Little evidence for a protective action of the vitamin against caries could be found, however, by Rosebury and Karshan[286] or Shelling and Anderson.[287] Blackberg and Berke[288] noted a relationship in dogs between a deficiency in the vitamin and certain changes in the pulp, enamel and dentine which are poorly calcified.[289]

The use of irradiation in the treatment of hay fever and asthma finds some confirmation in the work of Rappaport, Reed, Hathaway and Struck,[290] who observed that Viosterol, in large doses, combined with pollen injections is more effective than either alone. Rappaport and Reed[291] found Viosterol without effect in three cases of infectious asthma and two of urticaria, but it did protect six hay fever patients. Favorable effects of vitamin D on eczema have been reported.[292]

The ability of ergosterol to sensitize the pneumococcus to lysis by saponin is destroyed by irradiation.[293]

Viosterol has neither antiseptic nor bactericidal properties.[294] Greene[295] in an extensive study, was unable to detect any effect of a deficiency in vitamin D upon the ability of animals to produce antibodies or to resist infections. This is also the conclusion of Hess.[296]

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[279] Steinbach, M. M., and Rosenblatt, M. B., *Am. Rev. Tuberc*, **31**, 35 (1935), *Chem. Abs.*, **29**, 4410 (1935).

[280] Levaditi, C., and Li, Y. P, *Compt rend. soc biol.*, **106**, 169 (1931), *Chem. Abs.*, **25**, 3382 (1931), Policard, A., Ravault, P., and Barral, P., *Compt. rend soc. biol.*, **104**, 633 (1930); *Chem Abs.*, **25**, 4916 (1931); Pachioli, R, and Mengoli, V., *Bol. Soc Ital. Biol. Sper.*, **6**, 448 (1931), *Chem Abs*, **26**, 764 (1932); Haubold, H, *Beitr Path Anat*, **89**, 633 (1932), *Chem. Abs*, **26**, 5660 (1932), Loewy, A., and Grüninger, W, *Z. Tuberk.*, **61**, 317 (1931); *Chem. Abs*, **26**, 6011 (1932); Crimm, P D., *Am. Rev. Tuberc.*, **26**, 112 (1932); Black, W. C., Desavitsch, E. C., Trevorrow, V. E., and Lewis, R. C., *Ibid.*, **28**, 699 (1933).

[281] DeJust, L. H., *Rev. actinologie physiotherap.*, **6**, 1 (1931); *Chem. Abs.*, **26**, 2793 (1932).

[282] Mellanby, E., *Brit. Dental J.*, **45**, 545 (1924).

[283] Mellanby, M., and Pattison, C. L., *Brit Med. J.*, **I**, 507 (1932); *Chem. Abs.*, **26**, 5127 (1932), Mellanby, M., *Brit. Dental J.*, **62**, 241 (1937)

[284] Agnew, M. C., Agnew, R G., and Tisdall, F F., *J. Am. Dental Assoc*, **20**, 193 (1933), *Chem. Abs.*, **28**, 5103 (1934).

[285] Anderson, P. G., Williams, C. H. M., Halderson, H., Summerfeldt, C, and Agnew, R G, *J. Am Dental Assoc.*, **21**, 1349 (1934), *Chem. Abs.*, **28**, 7314 (1934); Fish, E. W., *J. Physiol*, **84**, 272 (1935), *Final Report of the Committee for the Investigation of Dental Disease, His Majesty's Stationery Office, London*, **1936**; *Chem. Abs*, **31**, 3531 (1937); McBeath, E. C., *Am. J Public Health*, **24**, 1028 (1934); *N. Y. J. Dentistry*, **8**, 217 (1938); *Chem Abs*, **32**, 5874 (1938); McBeath, E. C., and Zucker, T. F., *J Nutrition*, **15**, 547 (1938).

[286] Rosebury, T., and Karshan, M., *Arch. Path.*, **20**, 697 (1935).

[287] Shelling, D. H., and Anderson, G. M., *J. Am. Dental Assoc*, **23**, 840 (1936), *Chem Abs.*, **30**, 5624 (1936).

[288] Blackberg, S. N., and Berke, J D, *J Dental Res.*, **12**, 349 (1932); *Chem. Abs.*, **26**, 5129 (1932).

[289] See also Templin, V. M, and Steenbock, H., *J Biol Chem*, **100**, 217 (1933); Schour, I., and Ham, A. W, *Arch. Path.*, **17**, 22 (1934), *Chem. Abs*, **28**, 2762 (1934)

[290] Rappaport, B. Z., Reed, C. I., Hathaway, M. L., and Struck, H. C., *J Allergy*, **5**, 541 (1934); *Chem Abs.*, **28**, 7361 (1934).

[291] Rappaport, B. Z., and Reed, C. I., *J. Am. Med Assoc.*, **101**, 105 (1933).

[292] Comel, M, *Giorn. ital. dermat.*, **76**, 89 (1935); *Ber. ges Physiol. exptl. Pharmakol.*, **88**, 59; *Chem Abs.*, **31**, 8629 (1937).

[293] Klein, S. J., *J. Bacteriol.*, **26**, 215 (1933).

[294] Montgomery, B. E., *Proc. Soc Exptl. Biol Med*, **28**, 481 (1930).

[295] Greene, M. R., *Am. J Hyg*, **17**, 60 (1933); *Chem. Abs.*, **27**, 1661 (1933).

Notwithstanding these generally negative results, there have been papers purporting to show that D increases the resistance to infection. Robertson and Ross [297] found rachitic rats receiving *B. enteriditis* orally showed a 5 per cent survival when the diet contained non-irradiated and 30 per cent survival when it contained irradiated whole wheat. Similar effects also were described as due to the direct irradiation of the rat through Vitaglass. Koboshi [298] found subcutaneous injections of staphylococci to produce more serious effects in rats deprived of vitamins A and D than in normal animals. Doses of Vigantol prevented the appearance of abscesses. Choun [299] believed a high-vitamin diet to increase the resistance of guinea pigs to diphtheria. Pfannenstiehl [300] noted a decreased germicidal power of the blood for typhoid organisms in D avitaminosis. Kemmler [301] found skin wounds to heal more rapidly when an irradiated ergosterol solution was applied directly. Pritchett [302] believed the resistance of mice on a normal diet to infection with paratyphoid bacillus or mouse typhoid bacillus to be increased by the addition of butter fat, cod-liver oil or by the use of irradiated milk.

It has been suggested that viosterol may be of value in the treatment of lead poisoning, since in cats large doses increase the excretion of that metal.[303]

Irradiated ergosterol is also asserted to increase the thrombocytes in blood and to reduce the coagulation time.[304] It, as well as ultraviolet irradiation, tends to produce an increase in the fibrinogen and a decrease in the antithrombin content of the blood of newborn infants.[305] Leopold, Bernhard and Tow [306] report the lipids of the blood of children to be increased after ultraviolet irradiation, although the lipoid-phosphorus content is not changed. Nakae,[307] finds in rabbits that the daily administration of 0.1 to 1.5 cc. of irradiated ergosterol preparations decreases the serum cholesterol by about 40% in a month. Blood catalase is increased by small doses but decreased by an excess of vitamin D, according to Jusatz.[308] Feeding moderate amounts does not affect the glutathione level in the blood, but after toxic doses, although the number of red cells is increased, each cell has a reduced glutathione content.[309]

It seems well established that metabolism is increased by vitamin D. Handovsky [310] found irradiated ergosterol to increase the oxygen consumption of liver sections *in vitro*. Dhar[311] has suggested that vitamin D may be essential to the proper oxidation of fats in the body. In infants with rickets or tetany, Nitschke and Schneider[312] observed a lowered metabolic rate, which could be made to rise by giving the vitamin. Reed, Thacker, Dillman and Welch[313] found large doses of irradiated ergosterol to increase the metabolic rate of normal dogs. Landelium and Ljungkvist[314] have confirmed the ability of the vitamin to increase the depressed oxygen consumption of rachitic rats. Reed[315] found the administration of 20,000 to 552,000 I.U. daily, as Viosterol, to rats in two to six days caused first a marked increase in the metabolic rate, followed by a decrease and an irregular return to normal. On the other hand, Massaroli,[316] using the metadinitrobenzene method, found irradiated ergosterol to slow down the oxidation-reduction processes of the tissues. An increase may be observed in the respiration of the skin, according to Presnell.[317] It is said that the injection of irradiated (but not of unirradiated) ergosterol into the gall bladder of guinea pigs causes adenoid growths.[318]

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[296] Hess, A. F, *New England J. Med.*, **207,** 367 (1932). See, however, Holm, R., *Z. Immunitats*, **82,** 479 (1934); *Chem Abs*, **28,** 7346 (1934). For a general review, see Clausen, S W., *Physiol Rev.*, **14,** 309 (1934), Robertson, E. C, *Medicine*, **13,** 123 (1934).

[297] Robertson, E. C., and Ross, J. R., *Proc. Soc. Exptl. Biol. Med.*, **27,** 999 (1930), **28,** 443 (1931).

[298] Koboshi, S., *J. Chosen Med. Assoc.*, **23,** 39 (1933); *Chem Abs.*, **28,** 4453 (1934)

[299] Choun, C. K., *Z. Immunitäts.*, **81,** 432 (1934), *Chem Abs.*, **28,** 5505 (1934).

[300] Pfannenstiehl, W., *Sitzsber. Ges. Beförder ges. Naturw. Marburg*, **67,** 71 (1932); *Chem. Abs.*, **28,** 5507 (1934).

[301] Kemmler, H., *Mitt. Grenzgeb. Med. Chir.*, **43,** 453 (1934); *Chem Abs*, **29,** 5927 (1935).

[302] Pritchett, I. W., *J. Exptl. Med.*, **46,** 557 (1927)

[303] Flinn, F. B., and Smith, A. R, *J. Ind Hyg.*, **15,** 156 (1933); *Chem. Abs*, **27,** 3529 (1933)

[304] Phillips, R. A, Robertson, D. F, Corson, W. C, and Irwin, G. F., *Ann. Int Med.*, **4,** 1134 (1931); *Chem. Abs.*, **25,** 5210 (1931).

[305] Sanford, H. N., Gasteyer, T. H., and Wyat, L., *Am J. Diseases of Children*, **43,** 566 (1932); *Chem. Abs.*, **26,** 3560 (1932); Babasaki, Y, *Folia Pharmacol. Japon.*, **14,** 1 (1932); *Chem. Abs.*, **26,** 4100 (1932).

[306] Leopold, J. S, Bernhard, A., and Tow, A., *Am. J. Diseases of Children*, **43,** 882 (1932); *Chem. Abs.*, **26,** 4350 (1932).

[307] Nakae, R., *Nagoya J. Med. Sci.*, **7,** 88 (1933); *Chem Abs*, **28,** 3457 (1934).

[308] Jusatz, H. J., *Klin. Wochschr.*, **11,** 1501 (1932); *Chem Abs.*, **27,** 1030 (1933).

[309] Hesse, H., *Biochem. Z.*, **268,** 304 (1934).

[310] Handovsky, H., *Arch. Exptl. Path. Pharmakol.*, **159,** 383 (1931); *Chem. Abs.*, **25,** 4053 (1931).

It has been stated that irradiated cholesterol accelerates alcoholic fermentation in brewing, although non-irradiated cholesterol inhibits it.[319]

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[311] Dhar, N. R., *J. Phys. Chem.*, **36**, 1846 (1932).

[312] Nitschke, A., and Schneider, M., *Z. Kinderheilk.*, **54**, 1 (1932); *Chem. Abs.*, **27**, 5399 (1933).

[313] Reed, C. I., Thacker, E. A., Dillman, L. M., and Welch, J. W., *J. Nutrition*, **6**, 355 (1933), *Chem. Abs.*, **27**, 5785 (1933).

[314] Landelium, E., and Ljungkvist, G., *Skand. Arch. Physiol.*, **68**, 252 (1934); *Chem. Abs.*, **28**, 4460 (1934).

[315] Reed, C. I., *Proc. Exptl. Biol. Med.*, **32**, 274 (1934).

[316] Massaroli, P., *Riv. pat. Sper.*, **10**, 1 (1933); *Chem Abs*, **28**, 3457 (1934).

[317] Presnell, A. K., *J. Biol. Chem.*, **121**, 5 (1937).

[318] Schmidt, H. O., *Z. Krebsforsch.*, **45**, 335 (1937); *Chem. Abs*, **31**, 5874 (1937)

[319] De Fazi, R., and Pirrone, F., *Ann. Chim. Applicata*, **21**, 419 (1931); *Chem Abs*, **26**, 799 (1932); Pirrone, F., *Ann. Chim. Applicata*, **22**, 731 (1932); *Chem Abs.*, **27**, 1916 (1933), Mameli, E., and Mossini, A., *Giorn. Chim Ind. Applicata*, **16**, **377** (1934), *Chem Abs.*, **28**, 7415 (1934)

Chapter 40

Commercial Production of Vitamin D

Rickets is now recognized to be an extremely widespread disease, its incidence being as high as 50 to 75 per cent. This is because milk, the chief food of the infant, is relatively low in antirachitic potency. Eggs and fish are practically the only foods which contain large amounts of the necessary food factor. Vegetables are entirely lacking in it.[1] For this reason, the discoveries described in the preceding chapters quickly found application in the preparation of infant foods, pharmaceutical products and in improving the dietetic value of milk. In the preparation of poultry foods, the various methods of introduction of the vitamin have been of great economic importance.

Notwithstanding the fact that the process of irradiation of foodstuffs was discovered in the United States, its widespread adoption, at least in the case of dried milk and the production of pharmaceutical solutions containing irradiated sterols, seems to have come about first in Germany, where György reported on the value of irradiated milk as early as 1926. The earliest commercial milk irradiation was conducted in Frankfurt by Scheer and in Basel by Wieland.[2] Irradiated Dryco has been manufactured in the United States since about 1927: Steenbock applied for a patent on June 30, 1924, and this was issued in the United States[3] and assigned to the University of Wisconsin Alumni Research Foundation. By 1929, this foundation had licensed five drug manufacturers to produce irradiated sterol preparations.[4] By November, 1929, the American Medical Association had approved the name Viosterol for such preparations. At about this time, licenses were also granted for the irradiation of milk and various cereal preparations. In England, a Steenbock patent[5] made mention of the possibility of harmful overirradiation and stated that this could be avoided by limiting the time of exposure. The patent also included the separation of non-saponifiable lipids from fats either before or after the irradiation and their incorporation into foods. This included the preparation and irradiation of sterols and their esters obtained from such plant materials as yeast, molds, mushrooms, ergot, various seeds and straw, as well as from brain and other animal sources. In other U. S. Patents,[6] he described the irradiation of cereals or solid cereal products to a regulated degree to develop antirachitic properties without subsequent injury to either these properties or to the palatability, by strictly limiting the time.

There are a number of other patents dealing with irradiation processes. Tillisch,[7] claimed that irradiation of oils and fats produced, in addition to the antirachitic vitamin, the fat-soluble A if oxygen was excluded. This is now known not to be possible. The harmful effects of ozone were eliminated through the use of a calcspar filter in the method of Heinemann,[8] and Scholl[9] attained the same objective when he displaced the air from an irradiated liquid by the passage of an inert gas. Stamsö[10] increased the antirachitic potency of food oils, such as peanut oil, intended for a butter substitute, by irradiating it in thin layers with the exclusion of air, or by immersing lamps in the flowing liquid for not more than an hour. This was reduced to ten minutes in a later patent.[11] In other patents, there were many indefinite claims for the improvement of food products, without particular mention of the development of antirachitic potency, although this was undoubtedly the objective intended; the claims related to various details of the methods employed. Pacini[12] used rays other than those in the ultraviolet range, particularly infrared rays, or, in another patent,[13] rays longer than 3022A for the treatment of many substances such as bacilli, molds, sarcoma tissue, and ergot, said to contain a growth vitamin.

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[1] Hess, A. F., "Rickets, including Osteomalacia and Tetany," p. 102, Philadelphia, Lea and Febinger, 1929.

[2] See also György, P., *Klin. Wochschr.*, **5**, 747 (1926); **4**, 1118 (1925).

[3] Steenbock, H., U. S. P. 1,680,818, Aug. 14, 1928, to Wisconsin Alumni Research Foundation.

[4] *Drug Markets*, **24**, 347 (1929).

[5] Steenbock, H., British P. 236,197, June 30, 1924; *J. Soc. Chem. Ind. Suppl.* **B**, 735 (1925), 314,942, July 5, 1928; *Chem. Abs.*, **24**, 1411 (1930).

[6] Steenbock, H., U. S. P. 1,871,135-6, Aug. 9, 1932, to Wisconsin Alumni Research Foundation; *Chem. Abs.*, **26**, 5675 (1932); German P. 605,960, Nov. 22, 1934, *Chem. Abs.*, **29**, 1862 (1935).

[7] Tillisch, H. C. E., British P. 270,296, April 28, 1926; *Chem. Abs.*, **22**, 1415 (1928).

During ultraviolet irradiation of foodstuffs, Ried[14] employed a simultaneous irradiation either with x-rays or with wave-lengths longer than ultraviolet. Kelly[15] similarly proposed the simultaneous or subsequent application of cathode rays. The use of the latter alone was claimed by Knudson.[16] Sperti[17] claimed the use of soft x-rays.

Perino[18] described the use of an alkali monohydrogen phosphate solution in conjunction with the ultraviolet irradiation of various types of vegetable material.

Another type of patent covered the use of only restricted wave-length regions within the ultraviolet range in order to control the processes in such a manner as to avoid the accumulation of undesirable products or the destruction of the vitamin once it had formed. Thus, Sperti, Withrow, Norris and Schneider[19] described a process for simultaneously increasing the vitamin content and destroying bacteria in which foods are irradiated with ultraviolet light with the exclusion, by suitable filters, of those shorter wave-lengths which are harmful to the taste, smell and color of the food. Chesney[20] places the threshold for destructive effects in the irradiation of foods at about 2900A and avoids the action of shorter wave-lengths by employing concentrated sunlight or skyshine. Bills[21] described an apparatus for exposing materials on a belt conveyor to sunlight filtered through a covering material such as Cellophane which is transparent to ultraviolet rays.

Reiter[22] used only radiations longer than 2800A in irradiating substances containing ergosterol to avoid the formation of toxic products. It is now recognized that this cannot be accomplished since D_2 itself has toxic properties, but the formation of other inert toxic substances can be lessened. Most of the patents dealing with the use of filtered radiations were applied for before or shortly after the appearance of the work of Reerink and van Wijk, discussed in the preceding chapter. A study of this will aid in the evaluation of claims for the action of specific wave-lengths. Reiter's claims were in part based upon his observation[23] that, in the irradiation of milk, it is the wave-lengths between 2400 and 2800A which cause the undesirable changes in odor and taste.[24]

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[8] Heinemann, F., German P 530,877, Nov. 4, 1926; *Chem Abs.*, **26**, 221 (1932)

[9] Scholl, H., French P. 646,792, Dec 28, 1927; *Chem. Abs*, **23**, 2106 (1929); British P. 283,472, Jan. 9, 1928; *Chem. Abs.*, **22**, 4015 (1928); Canadian P. 285,853, Dec. 25, 1928; *Chem. Abs*, **23**, 1231, 2330 (1929).

[10] Stamsö, K K., British P 246,473, Jan. 26, 1925, *Chem. Abs.*, **21**, 465 (1927).

[11] Stamsö, K. K., Swedish P. 72,502, Aug. 25, 1931; 72, 613, Sept. 8, 1931; *Chem. Abs.*, **27**, 3294 (1933).

[12] Pacini, A. J., British P. 296,053, Aug. 24, 1927; *Chem. Abs.*, **23**, 2252 (1929).

[13] Pacini, A. J., U. S P. 1,681,120, Aug 14, 1928, to C N. Richter; *Chem Abs.*, **22**, 3737 (1928)

[14] Ried, O., Austrian P. 121,657, Oct. 13, 1930, *Chem. Abs.*, **25**, 3130 (1931); see also for the preservation of foods in this way, the Fromray Co, British P. 325,824, *Chem. Abs*, **24**, 3952 (1930), German P. 551,290

[15] Kelly, T. D., British P 293,255, Nov. 28, 1927, *Chem Abs.*, **23**, 1698 (1929).

[16] Knudson, A., British P 292,926, June 24, 1927; *Chem. Abs.*, **23**, 1446 (1929).

[17] Sperti, G., U. S. P. 1,982,028, Nov. 27, 1934, General Development Laboratories, Inc.; *Chem. Abs*, **29**, 517 (1935).

[18] Perino, J., British P. 279,487, Oct 20, 1926; *Chem. Abs.*, **22**, 2799 (1928); German P. 535,411; U. S. P. 1,754,434, April 15, 1930

[19] Sperti, G., Withrow, R, Norris, R. ,and Schneider ,H., U S. P. 1,982,029, Nov. 27, 1934, to General Development Laboratories, Inc., *Chem Abs.*, **29**, 517 (1935). There is now available a vegetable oil solution of ergosterol prepared in this manner containing 10,000 units per gram Rider, T., Sperti, G, Goode, P., and Cassidy, H., *J Am. Med Assoc.*, **106**, 452 (1936).

[20] Chesney, J. W. D., U. S. P. 1,704,173; *Chem. Abs.*, **23**, 1967 (1929); British P. 310,802, April 30, 1928.

[21] Bills, C. E., U. S. P. 1,877,382, Sept 13, 1932; *Chem. Abs.*, **27**, 4 (1933).

[22] Reiter, T., French P. 697,367, Jan. 30, 1930; *Chem. Abs.*, **25**, 3131 (1931); British P. 342,500, Jan. 17, 1930.

The Philips Gloeilampenfabriken[25] proposed to increase the efficiency by filtering out wave-lengths shorter than 2700A by the use of a 10-mm. layer of a 5 per cent benzene solution, or *p*-xylene.

Campsie[26] eliminated infrared rays and used a cold quartz lamp giving chiefly the band 2537-2540A, the resonance lines of mercury, radiations which most authorities would agree would have to be very carefully limited in their application if destruction of the antirachitic substance is to be avoided.

The use of the carbon arc for irradiating foods was described by Chaney.[27] The formation of ozone which gives off-flavor, is particularly avoided by the use of electrodes[28] containing added iron or aluminum so that the energy emitted will have a high proportion of wave-lengths between 2000 and 3000A, with only a negligible portion shorter than 2000A.

It is not possible to discuss in detail the many patents dealing with the structural features of irradiation apparatus.[29]

Shumway[30] removes the husk or skin from a cereal such as wheat, corn, oats, rye, barley or rice, and separates any pulverulent material, after which the whole cereal kernels are irradiated. Dorcas[31] described the apparatus commonly used for irradiating such foods. A thin layer of the product an eighth of an inch deep flows on a moving belt before an ultraviolet lamp.

Jaeger[32] described a therapeutic product prepared by irradiating dry banana meal in thin layers.

Berndt and Creighton[33] treat an opaque food substance at rest by ultraviolet rays only long enough to render a fraction of it antirachitic. This is then mixed with the untreated portion, again irradiated, the mixing and irradiation processes being alternately repeated, the total treatment received during the exposures of the fractions being less than the time required to impart undesirable properties to any portion.

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[23] Reiter, T., *Naturwiss.*, **17**, 876 (1929); Kisch, E., and Reiter T., *Strahlentherapie*, **39**, 452 (1930-31); Genin, G., [*Lait*, **17**, 47 (1937); *Chem. Abs.*, **31**, 7494 (1937)] avoids rays less than 2600A.

[24] See also Weckel, K. G., Jackson, H. C., Haman, R., and Steenbock, H., *Wis. Agr. Expt. Sta., Bull 435*, 68 (1936); *Chem. Abs.*, **32**, 2633 (1938).

[25] N. V. Philips Gloeilampenfabriken, British P. 343,528, Sept. 14, 1929; French P. 700,312; *Chem. Abs.*, **25**, 3776 (1931).

[26] Campsie, H. G., U. S. P. 1,980,971, Nov. 13, 1934; *Chem. Abs.*, **29**, 498 (1935).

[27] Chaney, N. K., U. S. P. 1,842,313, Jan. 19, 1932 (to National Carbon Co.).

[28] Chaney, N. K., U. S. P. 1,894,158; *Chem. Abs.*, **27**, 2504 (1933).

[29] Geffcken, H. H., and Richter, H., German P. 523,257, Feb. 8, 1927; 526,141, May 17, 1929; Goodall, F. E., and van Sant, R. H., U. S. P., 1,735,610, Nov. 12, 1930, N. V. Philips Gloeilampenfabriken, British P. 313,558, June 14, 1928; *Chem. Abs.*, **24**, 1036 (1930), Hickman, J. O., British P. 392,626, Feb. 17, 1932; Tixier, G., British P. 376,996, July 21, 1932; Ross, J. C., U. S. P. 1,896,379; Zecher, G., U. S. P. 1,929,910, Oct. 10, 1933; *Brit. Chem. Abs.* **B**, 587 (1934); Mailey, R. D., U. S. P. 1,969,655, Aug. 7, 1934; Ban, N., van Recsey, N., and van Recsey, E., British P. 382,349, Oct. 27, 1932, Brown, G., British P. 294,502, July 22, 1927, *Chem. Abs.*, **23**, 1967 (1929); Stephens, H. C., and Hoar, S. B., U. S. P. 2,020,250; Salmony-Karsten, A., *Allgem. Oel-und Fett-Z.*, **32**, 358 (1935); Beardslee, F. C., U. S. P. 1,682,318; Linder, J., Austrian P. 125,772, July 15, 1931; Soc. anon. des usines Rémy, Belgian P. 386,419, March 31, 1932; *Chem. Abs.*, **27**, 1416 (1933).

[30] Shumway, E. D., U. S. P. 1,928,397 (to Quaker Oats Co.), *Chem. Abs.*, **27**, 5840 (1933).

[31] Dorcas, M. J., *Food Industries*, **1**, 504 (1929); *Chem. Abs.*, **32**, 4508 (1929)

[32] Jaeger, C., British P. 290,195, April 18, 1928; *Chem. Abs.*, **23**, 916 (1929).

[33] Berndt, E. C., and Creighton, H. M., U. S. P. 2,072,416-7-8 (to R. U. V. Engineering Corporation); *Chem. Abs.*, **31**, 773, 2701 (1937).

A process for making biscuits, cakes, etc. in the presence of ultraviolet light was described by Elias,[34] and an apparatus for irradiating bread was described by Kielwein.[35] McGroarty[36] proposes the irradiation of an emulsified mixture prepared from salt, sugar, milk, shortening and yeast. This is then to be mixed with an irradiated yeast suspension, flour and water, for preparing bread dough. Antirachitic biscuits, prepared either from a dough with an added vitamin D concentrate or by the irradiation of the biscuits, retain their potency even after baking at 180-200°C. according to Markar'yan.[37] Tisdall[38] prepares biscuits, cakes, rusks or breads containing vitamins A, B, E and D from bone meal, baking powder and irradiated wheat germ, whole wheat and yeast.

Detailed studies of the antirachitic potency imparted to soda crackers by exposures at 12 inches, from a mercury arc emitting 94 ergs per second per sq. mm. have been reported by Read and Bailey.[39] Activation was attained in ten seconds, according to the results of bone-ash data on animals which had been on diets containing the crackers at a 20 per cent level. In the preparation of the crackers, lard, which may contain an appreciable amount of vitamin D, was replaced by hydrogenated shortening or lards shown to lack the vitamin. It was also shown that crackers made with irradiated shortening carried their antirachitic potency through the fermentation and baking processes.

Greaves and Nielson[40] find that the addition of 0.5 gm. of irradiated Utah-grown wheat causes a slight healing in rachitic rats This becomes pronounced with 0.75 gm. or with 1.25 gms of the unirradiated wheat. The highest provitamin content was found in the Baart and the lowest in the Kharkov varieties. Becker[41] studied the amounts of the vitamin which could be produced per hour in wheat, rye, barley, corn, peanut, linseed, sunflower-seed and pumpkin-seed meals. With the feed stationary, and exposures of 10 to 120 seconds, 160 to 1360 units were produced and in feed moving beneath the lamp in a thin layer, 1500 to 18,000 I U. A reasonable speed is that allowing an activation of about 0.5 I.U. per gram.

The addition of 10 per cent of irradiated farina in the diet of the rat failed to cause healing of rickets in experiments by Schlutz and Ziegler.[42] Pincussen[43] believes that irradiated oats stimulate carbohydrate metabolism in rabbits. The administration of irradiated cereals to school children produced no increase in calcium and phosphorus retention beyond the limits of normal variation, according to Porter-Levin.[44] Drake and Tisdall[45] found that irradiated farina given to children on a low calcium diet caused an increased efficiency in the utilization of these elements. Autoclaving an irradiated ration for six hours at fifteen lbs. does not affect its antirachitic properties.[46]

Ultraviolet rays impart antirachitic value to lettuce, alfalfa, spinach and soybeans, but not to cabbage.[47] Greater antirachitic properties are imparted to the cut than to the intact plant, but the exposures necessary to produce the vitamin in the plant are longer than those required to produce enough to protect a directly irradiated animal.

The irradiation of three kinds of mushrooms, as well as of the autoclaved, dried and ground pad resulting from the growth of certain molds in an inorganic medium containing 4 per cent of glucose, produces the vitamin, according to Preuss, Peterson, Steenbock and Fred.[48]

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[34] Elias, O. A., British P 266,101, Jan. 12, 1926

[35] Kielwein, F., German P 564,401, Nov 1, 1927; 608,277, Jan 19, 1935; *Chem Abs.*, **29**, 2618 (1935); German P. 647,522, July 6, 1937; *Chem Abs*, **31**, 8739 (1937)

[36] McGroarty, W J, U. S. P. 1,863,277; *Chem Abs.*, **26**, 4111 (1932)

[37] Markar'yan, E. A., *Proc. Sci. Inst. Vitamin Research, U S S R*, **1**, 198 (1936); *Chem Abs.*, **31**, 1854 (1937).

[38] Tisdall, F. F, British P. 357,223, Jan 24, 1930; *Chem Abs*, **27**, 350 (1933).

[39] Read, J. W, and Bailey, C. H., *Cereal Chemistry*, **10**, 99 (1933); *Chem. Abs.*, **27**, 2982 (1933); Wŏrner, A., [U. S. P. 1,796,134; *Chem Abs.*, **25**, 2493 (1931)] claims to avoid impairment of the taste of bread by using a reflector and permitting no direct rays to strike the bread

[40] Greaves, J E., and Nielson, H., *Food Research*, **1**, 495 (1936); *Chem. Abs*, **31**, 2647 (1937).

[41] Becker, J, *Mezogazdasági Kutatások*, **9**, 191 (1936); *Chem Abs.*, **30**, 7701 (1936).

[42] Schlutz, F. W., and Ziegler, M. R, *J Am Med Assoc.*, **93**, 1466 (1929); for further experiments on irradiated cereals, see Steenbock, H, Black, A., and Thomas, B. H, *J Biol Chem.*, **85**, 585 (1930).

[43] Pincussen, L, *Strahlentherapie*, **51**, 685 (1934), *Chem Abs*, **29**, 4051 (1935).

[44] Porter-Levin, T., *J Am. Diet. Assoc.*, **8**, 482 (1933); *Chem. Abs.*, **27**, 2986 (1933)

[45] Drake, T., and Tisdall, F. F., *Canadian Med. Assoc J*, **26**, 296 (1932); *Chem Abs.*, **27**, 4278 (1933).

[46] Daniels, A. L., and Jordan, D. P., *Proc. Soc. Exptl Biol Med*, **26**, 453 (1929).

[47] Loikin, M., *Contributions Boyce Thompson Inst.*, **3**, 245 (1931); *Chem Abs.*, **25**, 5450 (1931).

June butter fat is a poor source of vitamin D but is readily activatable, a ten-minute exposure at a depth of 1.6 mm. being best.[49] It would also be possible to improve its quality by the introduction of irradiated ergosterol. Lampitt, Sylvester and Bilham[50] have described a method for the irradiation of fats in which the light reaching the cell containing the fat is standardized by the use of a simultaneously exposed calibrated photoelectric cell. This arrangement, although employed for the study of oxidation processes, would also be applicable to the formation of the vitamin.

Nomura[51] proposed to ferment mixtures of flour, fruit juices, Japanese yams, and meat or fish soup, and then irradiate, dry and powder the product.

Favorable results with irradiated chocolates were reported by Krasso.[52] McKinlay[53] exposed chocolate candy on an endless belt to a mercury arc. Ried[54] ascribed beneficial effects to the irradiation of added metals or compounds such as zinc oxide, ferrous carbonate or calcium carbonate mixed with the fatty materials in the chocolate.

Labbé[55] extracted sterols from cacao beans, separated the α- and β- sterols by crystallization, mixed and irradiated them.[56]

Drummond,[57] in discussing the public health aspects of the vitamin D fortification of foodstuffs, concludes that their promiscuous irradiation is of questionable value. He did, however, consider the addition of calciferol to milk to be justified. Another discussion involving the status of the problem of vitamin addition to foods in general use has been given by Sherman and others.[58] The possibilities of the production of vitamin D have been extended by extravagant claims. Thus, it has been proposed to impregnate textiles with materials which, upon irradiation, acquire therapeutic properties.[59]

Pharmaceutical Developments. The value of pharmaceutical preparations of D_2, Viosterol, is firmly established, and, since its use is less apt to be promiscuous, is less subject to criticism than is the general irradiation of foodstuffs. At first it was believed that the antirachitic or growth-promoting properties of cod-liver oil could be enhanced by irradiation,[60] but, as stated in the preceding chapter it is now generally recognized that the oil contains little, if any, provitamin and the effects of irradiation can only be to destroy the vitamins A and D_3 naturally present.[61] However, Coster and Günther[62] maintained that the antirachitic potency once destroyed in the hardening of cod-liver oil may be restored by irradiation.

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[48] Preuss, L. M., Peterson, W. H., Steenbock, H., and Fred, E. B., *J. Biol. Chem.*, **90**, 369 (1931).

[49] Steenbock, H., Wirick, A. M., and Rising, B. M., *J. Dairy Sci.*, **13**, 497 (1930); *Chem. Abs.*, **25**, 729 (1931).

[50] Lampitt, L. H., Sylvester, N D., and Bilham, P., *Biochem. J.*, **29**, 1167 (1935).

[51] Nomura, R., French P. 701,808, Sept. 9, 1930; *Chem Abs.*, **25**, 4068 (1931).

[52] Krasso, H., *Wiener Klin. Wochschr*, **42**, 898 (1929); *Chem. Abs.*, **23**, 5238 (1929).

[53] McKinlay, D., British P. 276,860, Oct. 27, 1926; *Brit. Chem. Abs.*, **B**, 858 (1927); see also Oppenheim, E., British P. 309,601, April 13, 1928, Swiss P. 142,862, April 9, 1929; French P. 672,318, March 29, 1929; *Chem. Abs.*, **24**, 2213 (1930).

[54] Ried, O., British P. 316,264, July 26, 1928, *Chem. Abs.*, **24**, 1683 (1930); *Wiener Klin. Wochschr.*, **42**, 896 (1929); *Chem. Abs*, **23**, 5218 (1929); Austrian P. 126,148, Aug. 15, 1931; 123,648, Dec. 15, 1929.

[55] Labbé, H., French P. 700,036, Nov. 16, 1929; *Chem. Abs.*, **25**, 3409 (1931).

[56] See also for chocolate irradiation, the patents of the van Houten Co., British P. 340,580, Nov. 24, 1928; French P. 68,093.

[57] Drummond, J. C., *Chemistry and Industry*, 744 (1935).

[58] *Am. Public Health Assoc. Yearbook*, 78 (1933-4). For the engineering aspects, Gunderson, F. L., *Cereal Chem.*, **7**, 449 (1930); *Chem Abs.*, **25**, 131 (1931). Krauss, E, and Bethke, R. M., [*Ohio Agr. Expt. Sta., Bimonthly Bull*, **184**, 3 (1937); *Chem. Abs.*, **31**, 5886 (1937)] believe the addition of the vitamin to foods should be limited to milk. See also Fleisch, A., *Presse méd.*, **45**, 1542 (1937); *Chem. Abs.*, **32**, 3797 (1938); Knapp, A. W., *Chemistry and Industry*, 558 (1938)

[59] Lederer, B., French P. 796,046, March 27, 1936; *Chem. Abs.*, **30**, 5727 (1936).

[60] Price, W. A., *Am. J. Diseases of Children*, **33**, 78 (1927).

[61] Van Leersum, E. C., *Nederland. Tijdschr. Geneesk.*, **74, I**, 899 (1930); *Chem. Abs.* **24**, 3264 (1930).

[62] Coster, J. H., and Günther, G., Austrian P. 124,892, May 15, 1931; *Chem. Abs.*, **26**, 761 (1932).

In England, the production of ergosterol on a large scale was begun about 1928 by the British Drug Houses, Ltd. and by the Boots Drug Co., Ltd.[63] When irradiated, it was employed in margarine manufacture and in pharmaceutical preparations, such as Radiomalt, a palatable preparation which also contained vitamins A and B, and Vitamalt.[64]

Many of the patents cited in previous paragraphs apply also to the irradiation of ergosterol, but many more are concerned with this alone. Indeed, most of the developments discussed in the preceding chapter were patented. In the earlier period there were several claims which have since turned out to have little significance, or to be erroneous. The use of x-rays, cathode rays or corona discharges [65] apparently has not yet been widely applied. Claims have been made that the formation of the vitamin could be effected without the use of ultraviolet rays by treating ergosterol with metallic catalysts, such as copper, bronze and nickel.[66]

It is not possible to discuss the structural details of apparatus utilized for irradiation. At one time it was stated that the irradiated solutions should be at temperatures above 70°C.[67] Bills [68] gave details of a method for repeatedly circulating the solution through a chamber between the quartz mercury burner and the lamp casing. Fraps [69] described methods used in exposing ergosterol to sunlight.[70]

Trufanov [71] agitates the solution of ergosterol in a water-cooled quartz vessel by a flow of carbon dioxide sucked through by a vacuum pump. He alters about 50 per cent of a 2 per cent solution of the sterol in benzene, using as a source a carbon arc at a distance of 5 cm., the electrodes being composed of 65 parts carbon, 2.5 iron and 32.5 magnesia.

From and others claim [62] that infrared rays assist the formation of the vitamin by antibacterial rays from a glow discharge. They also provide means for circulating ozone. In addition, the use of dyes as sensitizers [73] has been proposed, although these substances have been said to lead to the formation of substances different from the vitamin by Windaus (chapter 39).

Apparently, the earliest commercial irradiated ergosterol product was the toxic Vigantol (chapter 39), prepared by the aid of a photoelectric device which cut off the light when the maximum absorption of wave-lengths between 2400 and 2500A had been attained.[74]

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[63] Langton, H. M., *J. Soc. Chem. Ind.*, **48**, 31 (1929).

[64] Reviews of recent applications· Tabern, D. L., *Clin. Med. Surg.*, **40**, 9 (1933); Weidlich, G, *Z. Vitaminforsch.*, **2**, 253 (1933), Tanret, G., *Bull. soc. chim. biol.*, **15**, 1346 (1933); Routh, I. B, *J. Chem. Educ.*, **10**, 13 (1933); Borgeaud, P., *Bull. Soc. Vaud. Sci. Nat.*, **58**, 17, 232 (1933).

[65] I. G. Farbenindustrie, British P. 318,269, April 2, 1928; *Brit Chem. Abs.* **B**, 711 (1929), Whittier, C. C., U. S. P. 2,106,779, 2,106,780-1-2, Feb 1, 1938, *Chem Abs*, **32**, 2692 (1938), Kramer, B., Natelson, S., and Sobel, A. E., U. S. P. 2,112,242, March 29, 1938, *Chem. Abs*, **32**, 3913 (1938); Milas, N. A., U. S. P. 2,117,100, May 10, 1938, *Chem. Abs.*, **32**, 5161 (1938) The product known as Ertron is made by the Whittier process.

[66] Heilbron, I. M., British P. 318,268, March 2, 1928, *Chem. Abs.*, **24**, 2244 (1930).

[67] I. G. Farbenindustrie, British P. 316,803, Sept. 17, 1928; *Chem. Abs.*, **24**, 1938 (1930).

[68] Bills, C. E., U. S. P 1,808,760, June 9, 1931, *Chem. Abs.*, **25**, 4156 (1931).

[69] Fraps, R. M., U. S. P. 2,015,264-5, Aug. 24, 1935; *Chem. Abs.*, **29**, 7587 (1935).

[70] Other patents on irradiation apparatus Buhtz, E., German P. 514,992, June 27, 1926, Cuny, L, German P, 637,716, Nov. 3, 1936, O'Brien, B, British P, 459,043 and 459,118 ,Dec 28, 1936, *Chem Abs.*, **31**, 4021 (1937); Pferdemenges, H., British P. 638,338, July 27, 1927, Patent Treuhand Ges. fur Elektrische Glühlampen, German P. 553,016, Dec 21, 1927, 541,991, Oct. 30, 1927, Quarzlampen. Ges., British P. 295,023, Aug 4, 1927; Nicholls, H. J., U. S. P. 2,070,307, *Chem. Abs*, **31**, 2054 (1937), Tixier, G., British P. 356,083, Jan. 22, 1930; Zecher, G., U. S. P. 1,929,910, Vilenkin, M, Russian P. 25,652, March 31, 1932; *Chem. Abs.*, **26**, 5231 (1932); Hickman, J. O., British P. 392,626, May 25, 1933; Salmony-Karsten, A., *Kautschuk*, **10**, 55 (1934); *Milchwirtschaft Zentr.*, **63**, 225 (1934); *Chem Abs.*, **29**, 236 (1935); Robinson, F. W., and Larsen, C. J., U. S. P. 2,051,395, Aug. 18, 1936.

[71] Trufanov, A. V., *Khim. Farm. Prom.*, 196, 253 (1933); *Chem. Abs.*, **28**, 498, 4108 (1934).

[72] From, V. C., Rowley, C. D., and Larsky, A. W., British P. 325,824, Feb. 2, 1929.

[73] Merck, Chemische Fabrik, British P. 286,065, March 8, 1927, *Brit Chem Abs.*, **B**, 836 (1928), *Chem. Abs.*, **23**, 483 (1929).

[74] British P. 296,093, Aug. 22, 1928, to I. G. Farbenindustrie A.-G.; *Brit Chem. Abs.*, **B**, 73 (1929)

Some have attempted to prevent losses during the irradiation by the use of certain additions to the solvent. Thus, ethylene or an alkali hydroxide has been added to ether or alcohol for this purpose.[75] Brauchli [76] uses hydroquinone or other dihydroxyphenols. To obtain stable solutions, Hooper [77] dissolves the highly active transformation product of ergosterol in 1,2—,2,3—,1,3—or 1,4-butanediol or 2-methyl-1, 3-propanediol. A method has been described for extracting the reaction product from the solvent after its exit from the reaction chamber, followed by the introduction of fresh provitamin into the solvent in the reaction chamber so that the solvent may be used repeatedly.[78] The acid esters of sterols may be irradiated before they are converted into salts.[79]

Various methods have been proposed for separating the irradiation product. In one,[80] the unchanged ergosterol is separated by virtue of its small solubility in alcohol, acetone, etc. The separation is continued until the ergosterol shows a dextrorotatory power greater than 25° for the yellow line of mercury. The active material is obtained by distillation of the solvent. Light and Frey [81] carry out the irradiation in solvents such as diethylene dioxide, triethanolamine, ethyl acetate, etc., which have a much higher solvent power for the activated product than for the original ergosterol. Jendrassik [82] irradiated solid ergosterol in contact with a solution containing vitamin D or ergosterol. The solution formed was led away by dialysis and fresh solution continuously added.

Filters to eliminate various wave-lengths have been suggested. Some would remove, by a carbon disulfide filter, wave-lengths longer than 3000A, particularly the 3126 and 3132A lines of mercury, believing these to be harmful.[83]

The work of Reerink and van Wijk, discussed in the preceding chapter, has also been made the basis of patents assigned to the Philips Lamp Works.[84] This, it may be recalled, eliminates wave-lengths shorter than 2700 and longer than 3000A.

Spectrographic control of the irradiation process is specified by Zimmermann and Frankenburger [85] much as in the earlier Vigantol patents, except that it is stated that the irradiation is to be interrupted before the maximal absorption between 2300 and 3000A has been exceeded.

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[75] I. G. Farbenindustrie A.-G., British P. 321,992, Oct. 25, 1928; *Chem. Abs.*, **24**, 2837 (1930); British P. 316,803, Sept. 17, 1928; *Brit. Chem. Abs.*, **B**, 836 (1929); *Chem. Abs.*, **24**, 1938 (1930).

[76] Brauchli, E., U. S. P. 1,824,653, Sept. 22, 1931 (to Hoffman LaRoche, Inc.), *Chem. Abs.*, **26**, 181 (1932), British P. 334,002, July 1, 1929.

[77] Hooper, C. W., U. S. P. 2,030,792 (Winthrop Chemical Co.); British P. 436,713, Oct. 16, 1935; *Chem. Abs.*, **30**, 1949, 2326 (1936)

[78] I. G. Farbenindustrie A.-G., British P. 314,267, Aug. 20, 1928; Frankenburger, W., and Weizel, W., German P. 491,222, May 20, 1928; *Chem. Abs.*, **24**, 2056 (1930); French P. 675,558, May 10, 1929, *Chem. Abs.*, **24**, 2674 (1930); see also Merck, German P. 556,716, March 6, 1928, for a description of an aqueous, colloidal solution of irradiated ergosterol

[79] Hoffman-La Roche Co., German P. 567,333, Dec. 13, 1928.

[80] Soc. des usines chimiques Rhône Poulenc, British P. 335,377, March 27, 1930; 335,277, June 25, 1929, French P. 698,040, June 11, 1930; *Chem. Abs.*, **25**, 1562, 3039 (1931).

[81] Light, R. F., and Frey, C. N., U. S. P. 1,955,554, (to Standard Brands), *Chem. Abs.*, **28**, 3752 (1934); British P. 394,408, June 29, 1933, Canadian P. 333,281, June 13, 1933, *Chem. Abs.*, **27**, 4631 (1933)

[82] Jendrassik, A., Hungarian P. 104,227, April 14, 1931; *Chem. Abs.*, **27**, 1387 (1933).

[83] N. V. Philips' Gloeilampenfabrieken, French P. 714,827, April 4, 1931; *Chem. Abs.*, **26**, 1715 (1932); French P. 737,234; May 17, 1932; *Chem. Abs.*, **27**, 1453 (1933); French P. 700,312, July 17, 1930; *Chem. Abs.*, **25**, 3776 (1931); **27**, 810 (1933); Dutch P. 32,096, Feb. 15, 1934; *Chem. Abs.*, **28**, 3842 (1934); French P. 708,548, Dec. 29, 1930; British P. 385,626, Dec. 20, 1932. Some of these deal with methods for removal of portions of the solvent and for the addition of added amounts of ergosterol.

[84] Reerink, E. H., and van Wijk, A., U. S. P. 1,904,751, April 18, 1933, to N.-V. Philips' Gloeilampenfabrieken, *Chem. Abs.*, **27**, 3560 (1933); German P. 634,146, Aug. 18, 1936; *Chem. Abs.*, **30**, 8533 (1936).

[85] Zimmermann, W., and Frankenburger, W., U. S. P. 1,896,191 (Winthrop Chemical Co.); *Chem. Abs.*, **27**, 2534 (1933).

Much of the work of the Göttingen laboratories has been patented, the United States patents being held by the Winthrop Chemical Co. Windaus [86] described the preparation of D_2 by irradiating ergosterol with light excluding wave-lengths shorter than 2750A. About 40-50 per cent conversion was obtained. Unchanged ergosterol was removed and the product was treated with citraconic anhydride for ten days in ether solution. Removal of the solvent was effected by evaporation at a low temperature. The residue is then saponified with alcoholic potassium hydroxide, diluted with water after about 12 hours, extracted with ether, petroleum ether or both, washed with water and dried. Following the latter operation, the solvent is evaporated and the residue crystallized from alcohol. Linsert [87] uses the unfiltered light of a magnesium spark, the remaining treatment being very similar to that described by Windaus. In the earlier patents, he specified the use of maleic anhydride, which left the antirachitic products in solution. Subsequently, Linsert [88] described the removal of the D_2 by the use of *m*-dinitrobenzoyl chloride in the presence of pyridine.

There are a great number of patents dealing with the introduction of irradiated ergosterol into food products. Ernotte [89] states that an aqueous-oil emulsion of vitamin D may be made with lecithin as the emulsifier.

The recent attention to a cholesterol derivative as the true provitamin of the natural antirachitic vitamin has been reflected in a patent by Waddell,[90] who described methods of treating cholesterol by mild oxidation with hydrogen peroxide or benzoyl peroxide, or by heat treatment, in order to increase the provitamin content.

The sterols of duck eggs may be irradiated to obtain preparations of antirachitic value for chickens.[91] Fats of various invertebrates may also be irradiated for this purpose.[92]

The various irradiated ergosterol preparations are very widely used,. Besides the simple vitamin D preparations, there are a great number of products in which the irradiated ergosterol is supplemented by various other vitamins. Practically all the preparations are assayed in terms of the international standard. During the early developments there were, however, considerable variations in the potency of the products, since they were assayed against samples of cod-liver oil, the potency of which was not guaranteed.[93]

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[86] Windaus, A., U. S. P. 1,873,942, Aug. 23, 1932; *Chem. Abs*, **26**, 6072 (1932); U. S. P. 1,902,745; *Chem. Abs.*, **27**, 3294 (1933), German P. 565,900, April 3, 1931, and 583,791, Sept. 9, 1933. The last describes the conversion of ergosterol to D_2.

[87] Linsert, O., U S. P. 1,902,785; *Chem. Abs.*, **27**, 3294 (1933); German P. 576,021 and 565,900; British P. 405,321; 370,743, April 2, 1931, to I. G. Farbenindustrie A.-G.; *Chem Abs.*, **28**, 4842 (1934).

[88] Linsert, O., German P 603,088, Sept. 22, 1934; *Chem Abs*, **29**, 552 (1935); U. S. P. 2,030,377; *Chem. Abs.*, **30**, 2326 (1936). The irradiation of 22-dihydroergosterol is also described. I. G. Farbenindustrie, A.-G., German P. 642,759, March 16, 1937; *Chem Abs*, **31**, 6417 (1937). U. S. P. 2,128,199, Aug. 23, 1938; *Chem. Abs*, **32**, 8702 (1938) For 7-dehydrocholesterol, see Windaus, A., and Schenck, F., U. S. P. 2,099,550, Nov. 16, 1937; *Chem. Abs.*, **32**, 312 (1938). German P. 661,686, June 24, 1938; *Chem. Abs*, **32**, 8706 (1938). For irradiation of oxidized cholesterol, E. I. du Pont de Nemours and Co., British P. 485,452, May 17, 1938; *Chem. Abs.*, **32**, 8081 (1938).

[89] Ernotte, M., French P. 796,101, March 30, 1936; *Chem. Abs*, **30**, 5676 (1936).

[90] Waddell, J., U. S. P. 2,028,364; *Chem. Abs.*, **30**, 1521 (1936); U. S. P. 2,056,992; *Chem. Abs.*, **30**, 8533 (1936). Pacini, A. J., U. S. P. 1,880,977-8; *Chem. Abs.*, **27**, 567 (1933) proposed the irradiation in the presence of a sensitizer such as uranium acetate. *Cf.* the work of Windaus on the course of such reactions with dyes as sensitizers.

[91] N. V. Philips' Gloeilampenfabrieken, British P. 464,066, April 12, 1937; *Chem Abs.*, **31**, 6417 (1937).

[92] N. V. Philips' Gloeilampenfabrieken, British P. 471,994, Sept. 15, 1937; *Chem. Abs.*, **23**, 1408 (1938); British P. 477,283, Dec. 22, 1937; *Chem. Abs*, **32**, 3913 (1938).

[93] See Holmes, A. D., and Pigott, M. G, *J. Biol. Chem.*, **64**, 263 (1925); Barnes, D. J., Brady, M. J., and James, E. M., *Am. J. Diseases of Children*, **39**, 44 (1930); De Sanctis, A. G., and Craig, J. D., *J. Am. Med. Assoc.*, **94**, 1285 (1930). For assays of German preparations, see Heubner, W., and Frerichs, M., *Arch. exptl. Path. Pharmakol.*, **165**, 553 (1932); *Chem. Abs.*, **26**, 5127 (1932).

METHODS FOR INCREASING VITAMIN D IN MILK.

Although rickets is not a fatal disease, it has serious consequences. Improved methods of treatment and a better understanding of the disease have lessened the number of cases in which obvious deformities have been produced. There remain many cases in which less evident skeletal changes of the chest may be produced which predispose to respiratory diseases and faulty development of the pelvic arch, the latter sometimes increasing the difficulties of childbirth. The high incidence of the disease has led to much recent work on the development of a safe, generally applicable prophylactic to be supplied in the nutrition of all infants of a community with the object of rendering subsequent treatment of the disease unnecessary. Since direct sunlight is not in all cases available in the winter months, and artificial irradiation of all infants is too expensive to be feasible, the vitamin must be supplied in the food. The only food given infants of the most susceptible age is milk, and for this reason it has been important to study its adequacy in the prophylaxis of rickets. Unfortunately, milk is low in antirachitic potency, having only about five to ten Steenbock units per quart, whereas an average infant requires 35 to 50, the equivalent of three teaspoons of cod-liver oil, in order to prevent the occurrence of rickets. According to Thomas and Cannon,[94] butter fat may contain about one Steenbock unit in 9 grams. Intensive work in the last few years has led to the proposal of a number of methods by which the antirachitic potency of milk may be rendered adequate.[95]

These may be classified as follows:

I. Treatment of the Cow
  A. Irradiation
  B. Addition of vitamin D to the food as
    1. Irradiated ergosterol
    2. Irradiated yeast
    3 Irradiated molds or other products
    4. Irradiated natural provitamin
    5. Concentrates from natural sources

II. Treatment of the Milk
  A. Addition of Vitamin D as
    1. Irradiated ergosterol
    2. Irradiated natural provitamin
    3. Concentrates from natural sources
  B. Irradiation

Antirachitic milk has the vitamin in an essential food which also supplies the necessary calcium and phosphorus.[96]

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[94] Thomas, B. H., and Cannon, C. Y, *Iowa Agr. Exp. Sta. Report*, 26 (1933), *Chem. Abs.*, **29**, 3002 (1935).

[95] General reviews are due to: Oser, B. L., *Milk Plant Monthly* **23**, No. 10, 34 (1934); *Chem. Abs.*, **28**, 7373 (1934); Tonney, F. O., *Am J. Public Health*, **26**, 665 (1936); Olson, T., and Wallis, G., *S. Dakota Agr. Exp. Sta*, *Bull. 296*, 3 (1935), *Chem. Abs.*, **30**, 5666 (1936), Andresen, O., *Arch. Kinderheilk.*, **90**, 65 (1930); *Chem. Abs*, **26**, 501 (1932); Weckel, K. G., *Milk Plant Monthly*, **23**, No. 3, 27 (1934); *Chem. Abs*, **28**, 3490 (1934); Roadhouse, C. L, *Proc 19th Ann Meeting, Western Division Am. Dairy Sci. Assoc.*, 109 (1933); Ellington, E. V., *Proc. 6th Ann State Coll Washington Inst. of Dairying*, 17 (1933); Batchelder, E. L., *Ibid.*, 48; *7th Inst.*, 47 (1934); Auerbacher, L. J., *Med. J Record*, Nov. 2, 16 (1932); Bunker, J, and Harris, R. S, *New England J. Med*, **211**, 1140 (1934); Shrader, J. H., *Arch. Phys. Therap. X-Ray, Radium*, **15**, 709 (1934); *Chem Abs*, **29**, 1861 (1935); Barnes, D. J., *Am. J. Diseases of Children*, **48**, 1258 (1934); Tobey, J. A., *8th Ann. Report N. Y. State Dairy and Milk Inspectors*, 107 (1934), *Chem. Abs*, **29**, 4465 (1935); Smith, C. A., *Milk Dealer*, **23**, No. 10, 38 (1934); McCollum, E V., *Ibid.*, **24**, No. 4, 32 (1935); Kon, S K., *J. Dairy Research*, **7**, 192 (1936); Kramer, B., and Gittleman, I. F., *New England Med. J.*, **209**, 906 (1933); Wyman, E. T., *Ibid.*, 889.

[96] Hess, A. F., *Am. J. Public Health*, **22**, 121 (1932).

That the potency of a milk depends upon the amount of sunlight to which the cow has access has been known since the first observations of the formation of vitamin D by irradiation.[97] Monthly assays conducted over a two-year period by Bechtel and Hoppert[98] indicated variations of as much as 900 per cent in antirachitic potency of the milk fats. The values were highest in July, August and September and lowest in February. Apparently, exposure to sunlight is the factor determining the activity of the milk. Guernsey milk varied from 4.8 to 43.8 U.S.P. units per quart and Holstein milk from 3.1 to 27.7. Gabathuler[99] states that milk at Davos in the Swiss Alps is twice as rich in D as milk from the plains.

Somewhat negative indications regarding the efficacy of irradiation of the cow were reported by Steenbock,[100] who was, however, concerned with the calcium balance of the lactating cow rather than with the antirachitic potency of the milk. Gowen, Murray, Gooch and Ames[101] reported that after daily exposures of cattle for fifteen to thirty minutes to ultraviolet rays, it was possible to cure rickets in chicks by feeding their milk. Similar results were reported by Falkenheim, Vöitz, and Kirsch.[102] Hess, Weinstock and Sherman[103] found irradiation of a nursing human mother to increase the antirachitic potency of her milk.

Irradiation of cows has been said also to increase the milk production by 4.77 per cent and the butter fat by 8.73 per cent.[104] Bünger,[105] however, was unable to observe significant changes in the amount of milk, its fat content, or mineral content or vitamin content in cows confined in stalls and irradiated either on the back, udders or both back and udders. The daily doses used varied from ten minutes at 100 cm. to thirty minutes at 75 cm. The irradiation period lasted about two months.

In experiments of Mitchell, Eiman, Whipple and Stokes,[106] carbon arcs were hung so that the arc formed opposite the under side of the cow's body about midway from front to back, providing a good exposure of the udders and more tender side of the body. The arcs were about 25 inches from the animals and at this distance the total ultraviolet intensity between 2000 and 4000A was 6400 microwatts per sq. cm. or 640 ergs per sq. mm. Each cow was irradiated for fifteen minutes each day on one side only. Rat assays gave an average of 22 units per qt. (controls 5 units per qt.) This milk had similar protective power on infants to irradiated milk, and appeared also to have curative power in florid rickets, although its action was somewhat slower than that of other antirachitic agents.

Hess pointed out that this method is suitable for carefully controlled herds producing certified milk. It may also be of value in smaller communities where large-scale equipment for the irradiation of milk appears to be too expensive.

It has been shown possible to increase the vitamin D content of butter fat by feeding the cow irradiated ergosterol.[107] The ergosterol need not, however, be isolated from the yeast before irradiation. Indeed, it has been stated that irradiated yeast is more effectively utilized.

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[97] Luce, E. M., *Biochem. J.*, **18**, 1279 (1924); Chick, H., and Roscoe, M. H., *Ibid.*, **20**, 632 (1926).

[98] Bechtel, H. E., and Hoppert, C. A., *J. Nutrition*, **11**, 537 (1936); *Chem Abs*, **30**, 6044 (1936); Campion, J. E, Henry, K. M., Kon, S. K., and Macintosh, J., *Biochem. J.*, **31**, 81 (1937).

[99] Gabathuler, A., *Z. Vitaminkunde*, 1 (1931); *Chem. Abs.*, **27**, 5102 (1933)

[100] Steenbock, H., Hart, E. B., Humphrey, G. C., Elvehjem, C A, and Scott, H T., *J. Biol. Chem.*, **67**, 371 (1926); Hart, E. B, Steenbock, H., and Scott, H. T., *Ibid.*, **66**, 441 (1925), **73**, 59 (1927).

[101] Gowen, J. W., Murray, J. M., Gooch, M. E., and Ames, F. B., *Science*, **63**, 17 (1926).

[102] Falkenheim, C., Vöitz, W., and Kirsch, W., *Klin. Wochschr*, **5**, 2071 (1926), *Chem. Abs*, **21**, 761 (1927).

[103] Hess, A F., Weinstock, M., and Sherman, E., *Proc. Soc. Exptl. Biol Med.*, **23**, 636 (1926).

[104] Iguchi, K., and Mitamura, K., *J. Faculty Agr. Hokkaido Imp. Univ.*, **24**, Pt. 2, 39 (1928); *Chem Abs.*, **23**, 2222 (1929).

[105] Bunger, H., *Zuchtungskunde*, **5**, 424 (1930); *Chem. Abs.*, **25**, 3409 (1931).

[106] Mitchell, J. M., Eiman, J., Whipple, D. V., and Stokes, J., Jr., *Am. J. Public Health*, **22**, 1220 (1932).

The irradiation of dried yeast was described by Kirsch.[108] Previously, there had been patents for the treatment of various yeast extracts. Feher[109] boiled yeast with alkali, mixed it with organic solvents and separated and crystallized the upper phase. The recrystallized material was irradiated in thin layers and incorporated into cocoa butter and pressed into tablets. The Merck Co.[110] proposed to treat only the non-saponifiable constituents of the yeast fat. MacLean[111] described an activated medical product obtained by incubating yeast in solutions containing phosphate and carbohydrate and subjecting the resulting sterols and fat to ultraviolet light. Autolyzed yeast has also been activated.[112]

The direct irradiation of layers of yeast about 0.1 inch thick at about a foot from a Hanovia burner was patented by Hall.[113] Favorable reports on the irradiation of beer yeast with wave-lengths 2970 to 3020A were rendered by Schübel and Gehlen.[114] According to Coward,[115] exposure to strong sunlight suffices. The ability of irradiated yeast to protect young rats has been repeatedly demonstrated, and the material retains its potency for months or even years.[116] Kon,[117] however, noted a toxic effect to follow the prolonged administration of this material at a 1 per cent level, although Matzko[118] did not observe this in the case of the use of customary amounts of a bakers' yeast irradiated to a potency of 5,000 to 10,000 units per gram.[119]

The daily administration of 500 I.U. of the vitamin in irradiated yeast during the five winter months to 69 normally growing infants protected them from moderate or marked rickets, and definite healing could also be effected within a month in marked rickets by this dose or its double.[120]

The addition of irradiated yeast to the diet of cows was not found to alter either the assimilation of calcium and phosphorus or the quantity or quality of the milk by Hart, Steenbock, Kline and Humphrey.[121] Kieferle[122] agreed that there is no increase in the milk yield, but found an increase in its D content and a shortening of the lapse in the lactation period. The melting point of the milk fat was increased slightly and there was a slight decrease in the refractive index and in the Reichert-Meissl number. Others, however, have claimed to find an increase in the secretion of milk.[123] Kroon[124] found the increase as much as

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[107] Thomas, B H, and MacLeod, F. L., *Science*, **73**, 618 (1931). Gerstenberger, H. J., and Horesch, A. J., [*J. Nutrition*, **5**, 479 (1932); *Chem. Abs*, **26**, 5616 (1932)] found that milk from cows receiving large daily doses (200,000 rat units) was only mildly antirachitic, 9 quarts being slightly less active than a teaspoonful of cod-liver oil.

[108] Kirsch, W., *Biochem. Z*, **196**, 294 (1928)

[109] Feher, G., Hungarian P. 100,696, Aug. 4, 1927; *Chem. Abs*, **25**, 2524 (1931).

[110] E. Merck Co., British P. 285,083, Feb 9, 1928, *Chem. Abs.*, **22**, 4726 (1928); *Brit. Chem. Abs.*, **B**, 264 (1929).

[111] MacLean, I. S, British P 295,757, May 23, 1927; *Brit. Chem Abs*, **B**, 797 (1928).

[112] Matsuoka, H., *Trans. Tottori Agr. Sci.*, **3**, 32 (1931); *Chem. Abs.*, **26**, 1645 (1932).

[113] Hall, P., British P. 354,371, May 8, 1930, *Chem. Abs*, **26**, 3870 (1932)

[114] Schübel, K., and Gehlen, W., *Arch. Exptl. Path. Pharmakol.*, **166**, 348 (1932); *Chem. Abs.*, **26**, 5611 (1932).

[115] Coward, K, *Lancet*, **II**, 920 (1933); *Chem Abs.*, **28**, 509 (1934)

[116] Vadimov, V., Voznava, A, and Semashko, V., *Elektrisikatzya Sel'skogo Khozyaistva*, **2**, No. 8, 20 (1932); *Chem. Abs.*, **27**, 1032 (1933).

[117] Kon, S. K., *Lancet*, **II**, 579 (1931); *Chem. Abs.*, **27**, 3242 (1933).

[118] Matzko, S. N., *Arch Tierernahrung Tierzucht.*, **9**, 623 (1933); *Chem. Abs.*, **28**, 6177 (1934).

[119] Sveshnikova, N. P., *Trans. Dynamics of Development (U.S S.R)*, **9**, 311 (1935); *Chem. Abs.*, **30**, 3032-3 (1936).

[120] Drake, T., Tisdall, F F., and Brown, A, *J. Nutrition*, **12**, 527 (1936); Drake, T., *Am. J. Diseases of Children*, **53**, 754 (1937) For Russian work on the value of various irradiated yeasts in poultry feeding, see Kratinova, E P, and Pokhil, A. I., *Problems Animal Husbandry (U S.S.R.)*, **1935**, No. 9, 93; *Chem. Abs.*, **30**, 2614 (1936); Zavadovskiĭ, M., Lepskiĭ, S., Kasheninnikova, A., Samokhvalova, G., and Balezin, P., *Trans. Dynamics of Development (U.S.S.R.)*, **9**, 269 (1935); *Chem. Abs.*, **30**, 3032 (1936).

[121] Hart, E. B., Steenbock, H., Kline, O. L., and Humphrey, G. C., *J. Biol. Chem.*, **86**, 145 (1930).

[122] Kieferle, *Proc. World's Dairy Congr. Copenhagen*, Sect. I, 166, 1931; *Chem. Abs.*, **27**, 755 (1933).

[123] Bilek, F., and Hynek, L., *Zemed Arch.*, **22**, 449 (1931); *Chem. Abs.*, **28**, 3447 (1934); Poelt, H., *Z. Vitaminforschung*, **1**, No. 4 (1932); *Chem. Abs.*, **28**, 1420 (1934).

[124] Kroon, H. M., *Milchwirtschaft Zentr.*, **60**, 325 (1932); *Chem. Abs.*, **26**, 3852 (1932).

25 to 30 per cent in the yield of milk as a result of feeding the yeast for three weeks after calving. Whatever may be true concerning the effect on the yield of milk, there have been many to show increases in the D potency when as much as 200 grams are fed daily.[125] Woelffer[126] found ten ounces of yeast of 30 D potency given daily to cows yielding thirty pounds of milk gave the milk a potency of 160 Steenbock units per quart. Yeast-fed cows require fifteen to twenty days to produce milk of the maximum potency, which is approximately 432 U.S.P. units per quart. High producers are more efficient than low producers in transferring the vitamin from the yeast to the milk. For efficient utilization, the yeast must be fed at least twice daily.[127]

Higher potencies can be produced by feeding irradiated yeast than irradiated ergosterol as the source of the vitamin.[128] At about 180,000 units per cow per day, the potency of the yeast-milk may reach 150 to 160 rat units per quart, whereas that after feeding an equivalent number of units of irradiated ergosterol contains only 120 to 130. At lower feeding levels, however, the two sources are comparable in their results, but only a slight increase in the potency of the milk results. When the ergosterol fed was increased to 300,000 units, less than 2 per cent of the units ingested appeared in the milk.

There is little doubt that the method is a practical one for enriching the milk, but it is not as cheap as the direct irradiation of the milk. Spickard[129] believes irradiated milk with but 50 to 60 units per liter as effective as yeast-milk with 160 units per liter.

It is also possible to feed the cow irradiated dried molds. Thomas and Cannon[130] find that this has its greatest effect during the first few days of the feeding. After this, there is a rapid decline in the amount of the D secreted. In general, they believe the cow very inefficient in transferring added vitamin D from her diet to her milk. It is, of course, also possible to add concentrates from liver oils or other natural sources to the diet of the cow.

Such concentrates are, however, more commonly added to the milk to avoid the inefficiency of the transfer.[131] Zucker[132] adds a cod-liver oil concentrate in the proportion of one part in 12,000 of milk and obtains probably 150 units per quart, equivalent to about three teaspoons of cod-liver oil. Post[133] described concentrates by which milk may be fortified to 1500 U. S. P. units per quart. Some ergosterol irradiation products have occasionally been suggested.

Yeast-milk is particularly of value on the certified farm where the ration can be thoroughly controlled.[134] It is scarcely applicable to the general supply of cities which may require thousands of farms to meet their demand. For this purpose, direct irradiation of the milk is the most suitable method. By this method

[125] Lepsky, S., *Z. Zücht. B., Tierzücht.*, **26**, 237 (1933); *Chem. Abs.*, **27**, 2987 (1933); Golf, A., and Seeling, K., *Biedermann's Zentr. B., Tierernahrung*, **6**, 65 (1934); *Chem. Abs*, **28**, 2036 (1934); Schieblich, M., *Biedermann's Zentr. B, Tierernährung*, **6**, 71 (1934); *Chem. Abs*, **28**, 2036 (1934).

[126] Woelffer, E. A., *Cornell Veterinarian*, **23**, 313 (1933); *Chem. Abs.*, **28**, 3109 (1934); see also Smith, C. A., *Milk Plant Monthly*, **23**, No. 5, 24 (1934); *Chem. Abs.*, **28**, 4458 (1934).

[127] Krauss, W. E., and Bethke, R. M., *Ohio Agr. Exp. Sta. Bimonthly Bull.*, **173**, 52 (1935); *Chem. Abs.*, **29**, 5525 (1935).

[128] Russell, W. C., Wilcox, D. E., Waddell, J., and Wilson, L. T, *J. Dairy Sci*, **17**, 445 (1934); *Chem. Abs.*, **28**, 5508 (1934).

[129] Spickard, V. W, *Northwest Med*, **33**, 204 (1934); *Chem. Abs.*, **29**, 4465 (1935).

[130] Thomas, B. H., and Cannon, C. Y., *Iowa Agr. Exp. Sta. Report on Agr. Research*, 49 (1934); 26 (1933); *Chem. Abs.*, **29**, 3002, 3375 (1935).

[131] Krauss, W. E., and Bethke, R. M., *Ohio Agr. Exp. Sta. Bimonthly Bull*, **162**, 77 (1933); *Chem. Abs.*, **27**, 4563 (1933); Krauss, W. E., Bethke, R M., and Wilder, W., *J. Dairy Sci.*, **16**, 549 (1933); Wyman, E. T., *New England J. Med.*, **209**, 889 (1933).

[132] Zucker, T. F., *Am. J. Public Health*, **23**, 10 (1933).

[133] Post, C. I., *Milk Dealer*, **24**, No. 3, 39 (1934); *Chem. Abs.*, **29**, 4843 (1935).

[134] Hess, A. F., Lewis, J. M., MacLeod, F. L., and Thomas, B. H., *J. Am. Med Assoc*, **97**, 370 (1931).

the milk acquires a potency of about 135 U.S.P. units per quart. An outstanding advantage of the method is the reduction of the human element of error to a minimum by the development of irradiation equipment, mechanically controlled. It is also possible that the provitamin in milk is that which on irradiation yields a product more suited to the human than that from ergosterol. Hess[135] early showed the effectiveness of irradiated dried milk in infant feeding, as well as of irradiated yeast.

Another advantage of irradiating milk is the fact that it contains but a limited quantity of the provitamin so that too high a potency cannot be attained, thus avoiding any danger of an overdose.[136] Its use also requires no coöperation on the part of the mother and eliminates the giving of cod-liver oil.

In 1925, Steenbock, Hart, Hoppert and Black[137] found it possible to increase the antirachitic potency of cow milk more than eight times by exposing it to a quartz mercury arc. That of goat milk could be increased twenty-four times. Milk irradiated on a large scale by the methods of Supplee and Dorcas has been extensively studied in the laboratory and clinic by Hess and Lewis[138] who find it a highly effective and reliable antirachitic agent. A quart or even less of the milk daily sufficed to protect infants from rickets, although this amount contained only 50 units as assayed by a standard rat method. The full explanation as to why smaller numbers of rat units are adequate when given in this form than in cod-liver oil has not yet been given. That it might be more effective than an equivalent number of rat units of irradiated ergosterol could be accounted for by a difference in the structures of the vitamins, the human differentiating between these although the rat does not. But presumably the natural vitamin in cod-liver oil is the same as that of milk so that the doses from the two sources which are equally effective on the rat should also be equally effective on the human. This assumption has, however, not yet been proved and it must remain an assumption until the vitamin has been isolated from irradiated milk and compared chemically with D_3. Other suggestions for the discrepancy may be offered. It may be related to the presence of other substances in the milk and in the cod-liver oil which alter the ease of absorption of the vitamin.[139] Supplee, Ansbacher, Bender and Flanigan[140] attribute the unexpected effectiveness of irradiated milk to the formation of a "symplex system" between the vitamin and a colloidal carrier such as lactalbumin. This they believe can form only in lipid-free lactalbumin. When lipids are present, the vitamin merely dissolves in the prosthetic group or lipid associated with the lactalbumin. This they suggest accounts also for the observation of Lewis[141] that vitamin D administered in the water phase with propylene glycol with accompanying milk constituents is more effective than when it is carried by an oil vehicle. Ansbacher and Supplee had found that about 18 per cent of the total milk cholesterol is associated with proteins, chiefly lactalbumin. It is to this prosthetically bound, cholesterol-like lipid, rather than to that free in the butter-fat, that they attribute the ability to form, on irradiation, a particularly effective antirachitic agent.

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[135] Hess, A. F., *J. Am. Med. Assoc.*, **89**, 337 (1927); see also Eddy, W. H., *Arch. Pediat.*, **44**, 320 (1927); Supplee, G. C., and Dow, O. D., *Am. J. Diseases of Children*, **34**, 364 (1927); *J. Biol. Chem.*, **75**, 227 (1927); **73**, 617 (1927).

[136] Mohr, W., Kulteren, S., and Richter, V., *Molkerei-Z., Hildesheim*, **45**, 545 (1931); *Chem. Abs.*, **26**, 3010 (1932).

[137] Steenbock, H., Hart, E. B., Hoppert, C. A., and Black, A., *J. Biol. Chem.*, **66**, 441 (1925).

[138] Hess, A. F., and Lewis, J. M., *J. Am. Med. Assoc.*, **99**, 647 (1932). An early German product—Hanauer milk—had an activity such that 100 cc. corresponded to 5-6 gram of commercial cod-liver oil. Bamberger, P., *Deut. med. Wochschr*, **55**, 1547 (1929); *Brit. Chem. Abs.*, **B**, 637 (1930).

[139] For evidence of the disparity of doses see, Hess, A. F., Lewis, J. M., McLeod, F. L., and Thomas, B. H., *J. Am. Med. Assoc.*, **97**, 370 (1931); Wyman, E. T., and Butler, A. M., *Am. J. Diseases of Children*, **43**, 1509 (1932); Gerstenberger, H., and Horesh, A., *J. Nutrition*, **5**, 479 (1932); Hess, A. F., and Lewis, J. M., *J. Am. Med. Assoc.*, **99**, **647** (1932); **101**, 181 (1933).

[140] Supplee, G. C., Ansbacher, S., Bender, R. C., and Flanigan, G. E., *J. Biol. Chem.*, **114**, 95 (1936); Ansbacher, S., and Supplee, G. C., *J. Biol. Chem*, **105**, **391** (1934).

[141] Lewis, J. M., *J. Pediatrics*, **6**, 362 (1935).

Before describing the methods employed by Supplee and others, brief mention will be made of the difficulties which must be overcome and of some of the methods proposed in Germany and elsewhere. The early attempts to irradiate milk were usually marked by a tendency to overirradiate it with resultant deterioration in odor and taste. Schultz [142] attributed this to the action of hydrogen peroxide upon the protein and found that this change did not parallel the production of the antirachitic potency. The irradiation of the cream alone did not affect the taste. He claimed that 15 grams of irradiated protein-free milk-fat cured rickets in children.[143] As yet, however, relatively little is known as to the nature of the deterioration due to overirradiation. Energy between 2600 and 3100A appears less active in flavor production than that of wave-lengths shorter than 2600A. The range from 3100 to 3800A is more active in causing flavor changes than that from 3800 to 7000A.[144]

Anderson and Triebold [145] passed milk through a commercial irradiator eight times and could detect no marked changes in the chemical composition or in the fat constants. Although the induction period for the oxidation of the fat was reduced from twenty to seventeen hours by irradiation, the rate of deterioration over a period of six months was unchanged. Digestion studies *in vitro* with pepsin and with trypsin indicated a slightly increased rate in the early stages due possibly to the destruction of an antienzyme. Hoffman [146] used a mercury-argon discharge tube which emits little heat radiation [147] in the effort to lessen the changes in taste. To overcome the difficulty of a lack of penetration of the milk by the effective rays (not over 0.1 mm.), he arranged to have it flow through an adjustable slotted distributor onto a cylindrical net of narrow-mesh wire in the center of which was placed the source. For treating raw milk, he conducted the process in the presence of an inert gas to avoid the destructive action of ozone on vitamins A and C.

Commercial milk irradiation appears to have been first carried out in Germany. It is not feasible to give the details of the apparatus there suggested.[148]

The Dry Milk Co.[149] proposed to spray the milk (liquid or powdered) before the source for a period as short as eight seconds which, with the intensities used, permitted the development of 75 per cent of the possible antirachitic potency before the formation of a disagreeable odor or taste. Most irradiate the milk in thin flowing films.[150]

Salmony-Karsten [151] believed it necessary to use an inert gas to exclude oxygen and also to add a means for cooling the milk during the process. Hickman and Hickman[152] pointed out that exclusion of air is unnecessary when the milk is exposed while flowing in a thin film on one side of a milk cooler. The irradiation is for a period of 8 to 30 seconds at a distance of 11 inches from a 2000 c.p. quartz mercury-vapor lamp with reflectors.

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[142] Schultz, O., *Milchw. Forsch.*, **4,** 37 (1927); *Chem. Abs.*, **21,** 3631 (1927).

[143] Schultz, O., *Klin. Wochschr.*, **6,** 848 (1927); Schultz, O., and Rohr F., *Deut. med. Wochschr.*, **33,** 1255 (1927).

[144] Weckel, K G., Jackson, H. C., Haman, R., and Steenbock, H., *Ind. Eng. Chem.*, **28,** 653 (1936).

[145] Anderson, A K., and Triebold, H. O., *J Dairy Sci*, **15,** 469 (1932); *Chem. Abs.*, **27,** 784 (1933).

[146] Hoffman, *Proc. 8th World Dairy Conference,* 460 (1928); *Chem. Abs.*, **23,** 5491 (1929).

[147] From, V. C., Rowley, C. D., and Larsky, A. W., British P. 346,682, Oct. 15, 1929, *Chem. Abs.*, 26, 537 (1932) specify the simultaneous use of infrared rays.

[148] Geffcken, H H, and Richter, H., German P. 557,334, March 19, 1927; 545,080, March 19, 1927; 545,886, Jan. 3, 1928, Löwenstein, L., German P. 552,263, June 6, 1928, *Chem. Abs.*, **27,** 353 (1933); Schindler, A., German P. 572,491, Feb. 8, 1927; Wiegand, K., German P. 541,991, Oct 30, 1927; 553,016, Dec 21, 1927; Ried, O, Austrian P. 116,463, Sept. 15, 1929; *Chem Abs.*, **24,** 2837 (1930); Kirsch, W., *Chem. Fabrik,* 150 (1928).

[149] British P. 298,585, June 11, 1927, to Dry Milk Co.; *Brit. Chem. Abs.*, **B,** 911 (1928).

[150] Trebler, H. A., U. S. P. 2,001,555; British P. 428,434, May 13, 1935. In this a single unit irradiates several flowing sheets of milk. Trebler, H. A., and Larsen, C. J., U. S. P. 2,018,332; British P. 432,011, July 18, 1935; see also Robinson, F. W., and Larsen, C. J., U. S. P. 2,051,395; Cuny, L., British P. 441,524, Jan. 21, 1936; Berndt, E. C, and Creighton, H. M., U. S. P. 2,065,054-5, *Chem. Abs.*, **31,** 773, 2701 (1937); Henszey, R. O., U. S. P. 2,060,865, *Chem. Abs.*, **31,** 1665 (1937).

[151] Salmony-Karsten, A., *Chimie et industrie,* **22,** 259 (1929); Chesney, J., U. S. P. 1,723,603, Aug. 6, 1929; *Chem. Abs.*, **23,** 4512 (1929) also excluded air.

Since it is a lipid that is the provitamin, the question has been raised as to whether it might not be better to irradiate the cream separately. Essig[153] found irradiated skimmed milk to be only slightly protective, although the same whole milk when irradiated was highly effective. Kersten and Schultz[154] irradiate the cream and then return it to the milk from which it had been separated. Recently, however, Supplee gave reasons for believing that the effectiveness depends in some manner upon an association of the vitamin with lactalbumin, so that the separation of the cream seems unnecessary. Furthermore, Dorcas and Supplee[155] find that under given irradiation conditions, the potencies which can be attained are not in proportion to the amount of fat present. Relatively high potencies are shown in samples with low amounts of fat. Krauss, Bethke and Washburn,[156] find, however, that as the fat percentage increases, the activatability is also increased. Still the solids-not-fat fraction of Holstein milk may contain more of the provitamin than that of Jersey milk, since the two milks can be activated to the same extent even though the Jersey milk contains more fat and has a higher original potency.

Hoefelmayr[157] described the irradiation of condensed, dried or curdled milk. Favorable results of clinical studies on the use of irradiated powdered whole milk were reported by De Sanctis, Ashton and Stringfield.[158] Weckel and Jackson[159] believed the most feasible method of irradiating milk was after evaporation of raw standardized milk at 208-210°F. until it contained 7.8 to 8.3 per cent of fat. The hot milk from the vacuum pan was then irradiated by a carbon arc by passage over a conical irradiator, after which it was homogenized, canned and sterilized. When diluted to the solid content of normal milk, the vitamin potency was 50 Steenbock units per quart, corresponding to 135 U.S.P. units. Cream could be successfully irradiated without the formation of undesirable flavors or chemical deterioration. Acids developed somewhat more slowly in irradiated than in untreated milk. Supplee, Bender, Flanigan, Dorcas and Greider[160] find, however, that the irradiation of evaporated milk does not result in as high a degree of potency as the irradiation of fluid milk when films of the same capacity* are subjected to the same intensity and quality of ultraviolet radiations. Since the films of the same capacity of evaporated milk are thicker and more dense than those of fluid milk, the penetration is correspondingly less. Greater antirachitic potency of evaporated milk may be attained by the exposure of thinner films for longer periods of time or by increasing the intensity of the source, but it still does not equal that attainable by the irradiation of fluid milk films. The degree of activation imparted to evaporated milk is not significantly different when homogenized and non-homogenized products are irradiated nor is it affected by varying the temperature between 55 and 165°F. The ultraviolet transmission is progressively decreased by preheating to 180°F., by concentration and by homogenization, as a result of physical changes in the inherent milk constituents.

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[152] Hickman, J. O., and Hickman, N. V., British P. 325,470, Sept 12, 1928; *Brit. Chem Abs.*, **B**, 484 (1930). See also Bragg, J. H., U. S. P. 1,954,065, April 10, 1934, *Chem. Abs.*, **28**, 3807 (1934).

[153] Essig, B, *Munch med Wochschr.*, **78**, 273 (1931); *Chem. Abs*, **25**, 4924 (1931).

[154] Kersten, G., and Schultz, O., German P. 577,531, June 1, 1933, *Chem. Abs.*, **28**, 541 (1934).

[155] Dorcas, M. J., and Supplee, G. C., *J. Dairy Sci.*, **17**, 433 (1934).

[156] Krauss, W. E, Bethke, R. M, and Washburn, R. G., *J. Dairy Sci.*, **19**, 739 (1936).

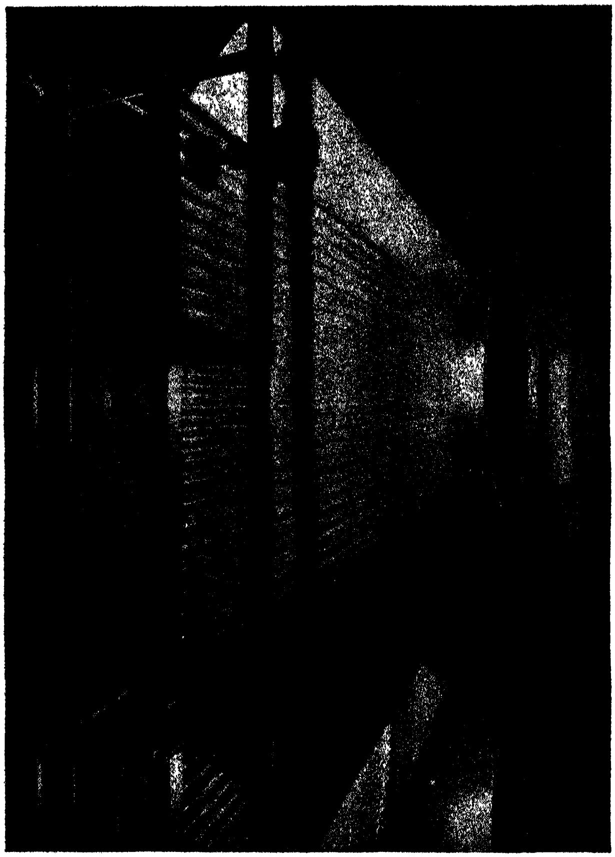
[157] Hoefelmayr, K., British P. 265,910, Feb. 12, 1926; *Chem. Abs.*, **22**, 468 (1928).

[158] De Sanctis, A G., Ashton, L. O, and Stringfield, O. L, *Arch. Pediat.*, **46**, 297 (1929); *Chem. Abs.*, **23**, 3956 (1929).

[159] Weckel, K. G., and Jackson, H. C., *Natl. Butter and Cheese J.*, **25**, No. 11, 24 (1934); *Chem. Abs.*, **28**, 5857 (1934); *Wisconsin Agr. Exp. Sta., Bull. 428*, 33 (1934); *Chem. Abs.*, **29**, 3052 (1935).

[160] Supplee, G. C., Bender, R. C., Flanigan, G. E., Dorcas, M. J., and Greider, C. E., *J. Dairy Sci.*, **19**, 67 (1936).

* The capacity is the film thickness times the distance of film travel.



Courtesy National Carbon Co., Inc.

FIGURE 156. Flat Type Milk Irradiating Unit.

From an engineering point of view the process has been studied most thoroughly by Supplee and co-workers. The most significant feature which has emerged under commercial conditions (treatment of 1000 lb. lots) is that the time of irradiation by either a quartz mercury-vapor lamp or a carbon arc need be but a few seconds, obviating changes in taste.[161]

The milk in 1000 lb. lots was exposed as a moving film (0.4 mm.) which received the rays at constantly changing angles of incidence varying from 0 to 90°. The

[161] Supplee, G. C., and Dorcas, M. J , *Lait*, 14, 1, 125 (1934); *Chem. Abs.*, 28, 3143 (1934); Supplee, G. C., U. S. P. 1,817,936, Aug. 11, 1931 (to Borden Co.); *Chem. Abs* , 25, 5477 (1931); Supplee, G. C., Dorcas, M. J., and Hess, A. F., *J. Biol. Chem*,, 94, 749 (1932)

complete cycle of exposure to the range of impingement angles required a period of about 0.3 second. The maximum potency was found to be attained within the first few seconds. Over 238 variations in the irradiation conditions were studied in this investigation.

There are two main types of apparatus which are employed in conjunction with the carbon arc, the flat and drum types (Figures 156 and 157). Units of various capacities have been employed. The capacity may be as low as 625 quarts per hour, and from these larger synchronized units may be assembled. A unit employed early by the Dryco Co.[162] had a normal capacity for the treatment of more than 5000 quarts per hour.

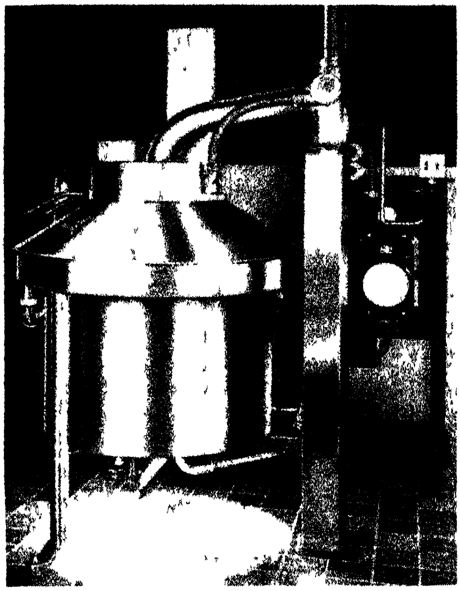


FIGURE 157.

National Type YN Milk Irradiating Unit

Courtesy National Carbon Co., Inc.

Supplee, Beck and Dorcas,[163] by comparing the quanta of energy applied per cc. with the molecules of vitamin D formed per cc. showed that the potency is dependent upon the amount of energy applied, provided that the radiations lie within the antirachitic range. It was immaterial whether the energy was from the Corex D filtered or unfiltered carbon arc or consisted of reflected rays only. This was true within the limits of energy of 409×10^3 ergs (545×10^{14} quanta) and 9486×10^3 ergs ($12{,}480 \times 10^{14}$ quanta). Mica screens which transmit practically no energy below 2900A and only 45 per cent at 3150A do not permit any source to increase the potency of the milk. The relative effectiveness of an equivalent amount of energy from different sources was in the following order: C carbon, Mg carbon, mercury arc and Sunshine carbon. When time and intensity were taken into account for practical purposes the effectiveness of the sources tested increased in the order: Mercury-vapor arc, Sunshine carbon arc, magnesium carbon arc and

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[162] Mitchell, J. M., Eiman, J., Whipple, D. V., and Stokes, J., Jr., *Am. J. Public Health*, **22**, 1220 (1932).

[163] Supplee, G. C., Beck, H. H., and Dorcas, M. J., *J. Biol. Chem.*, **98**, 769 (1932).

C carbon arc. The use of Corex D filters reduces the amount of energy reaching the milk per unit of time and causes a commensurate reduction in the rate of building up the potency. The effects of chromium-plated reflectors on the energy incident at normal incidence on milk at 61 cm. from an arc have been computed by Supplee, Hanford, Dorcas and Beck,[164] for the wave-length ranges 2,000-2,200A, 2,200-2,400A and 2,400-3,000A.

It was found by biological assays that the total quanta which must be applied to produce a plus-one line test in the rachitic rat was 5949×10^{15}. From the quantity of irradiated milk required and the assumptions that this must be equivalent to 0.03γ of D_2 and that its molecular weight is that of ergosterol, it was concluded that there had been produced 4.5×10^{13} molecules of the vitamin. (This implies that during the first few seconds when a definite amount of energy produces a definite amount of vitamin, the quantum yield is low, about 7×10^{-6}. Compare with the high quantum yields reported for the irradiation of ergosterol solutions, chapter 39. Evidently much of the energy is absorbed by other constituents of the milk). When the incident energy is increased beyond a certain point, $2{,}000\text{-}3{,}000 \times 10^{14}$ quanta per cc., little or no additional formation of vitamin occurs or destruction begins within very brief periods. The maximum concentration was reached after a total of about 2.5 million ergs per cc. had been applied. The concentration is then about 2.5γ per liter or practically twelve times that of the untreated milk.

The reflection of ultraviolet rays from the surface of milk is of the same order of magnitude as that from a water surface.[165] The degree of reflection increases as the angle of incidence decreases. At 75° and 45° incidence, about 3 per cent of the energy between 2550 and 3000A is reflected. At 30°, it is about 6 per cent, at 20° 13.4 per cent, 15° 28 per cent and from a 10° angle about 34 per cent. Milk films show selective reflection throughout the range of wave-lengths 2550 to 3300A, most pronounced at angles of incidence of 30° or less.

Only 20 to 40 per cent of the energy between 2500 and 2850A striking the surface of a milk film at right angles on a smooth quartz flowboard are transmitted by films 0.02 mm. thick.[166]

Films 0.11 mm. thick transmit 5 per cent or less of the incident energy within these limits. As the fat content of the milk is increased, the transmission is somewhat decreased. The transmission increases rapidly and progressively in the longer wave length region 2800 to 3300A

Under suitable conditions of high intensity, a high degree of activation can be obtained from exposures varying from less than a second to not more than two seconds. It is probable that the reaction occurs chiefly at the moving surface since extremely thin but slow-moving films showed a lower degree of activation after momentary exposure than did thicker but faster-moving ones. With high intensities it is also possible to produce measurable antirachitic properties in milk derivatives containing little or no butter fat.[167] Studies on the influence of various changes in film capacity, (that is film thickness × the distance of film travel), have also been reported.[168]

Whole milk irradiation units are made by the Cherry-Burrell Corporation, the Creamery Package Manufacturing Co.[169] and the Hanovia Co. (Figures 158 and 159).

[164] Supplee, G. C., Hanford, Z. M., Dorcas, M. J., and Beck, H. H., *J. Biol. Chem.*, **95**, 687 (1932).

[165] Supplee, G. C., and Dorcas, M. J., *J Dairy Sci.*, **17**, 607 (1934)

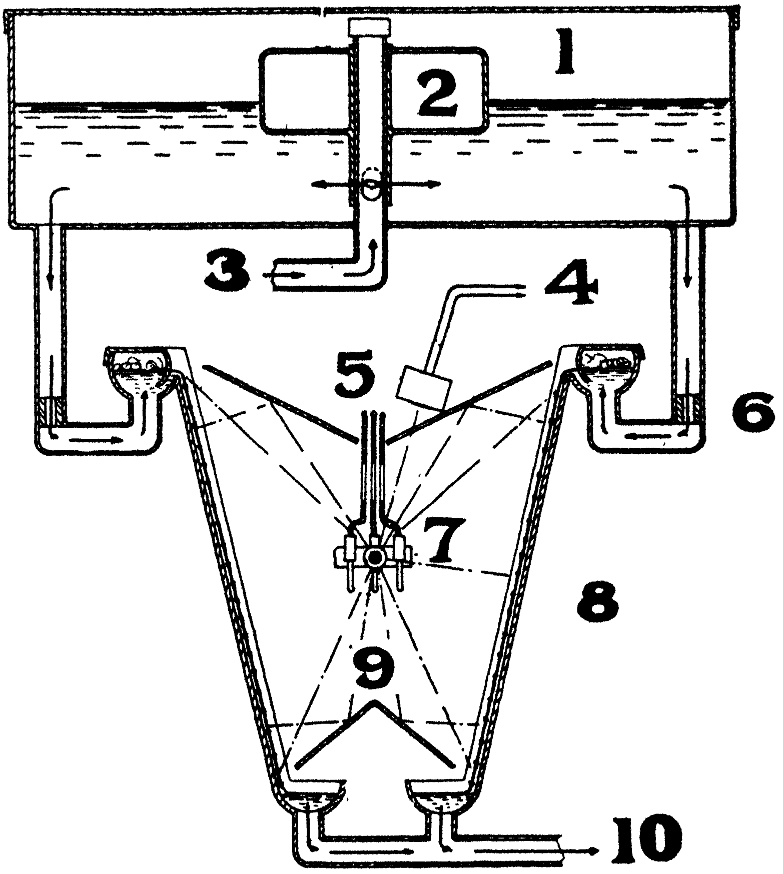
[166] Dorcas, M. J., and Supplee, G. C., *J. Dairy Sci.*, **17**, 433 (1934).

[167] Supplee, G. C., Flanigan, G. E., Bender, R. C., and Dorcas, M. J., *J. Dairy Sci.*, **17**, 483 (1934).

[168] Supplee, G. C., and Dorcas, M. J., *J. Dairy Sci.*, **17**, 527 (1934).

[169] British P. 450,341, July 15, 1936, to Creamery Package Manufacturing Co.

In these,[170] the milk is exposed while flowing on nearly vertical metal surfaces in thin films of about 300 to 350 lbs. per horizontal linear foot per hour. The effective distances traversed during exposure range from 9 to 60 inches in different types of equipment, using various sources and operating intensities. By means of a reflected light beam method, Beck and Weckel[171] determined the thickness at various horizontal levels of milk flowing by gravity in films of various capacities (lbs. per linear foot per hour) over vertical steel surfaces. At 200 lbs. per foot per hour or less, the films are of uniform thickness throughout their course of flow. At 300 lbs. per foot per hour, the thickness is variably greater in the first two or three inches of travel, but then becomes uniform. Under these conditions, the motion is accelerated at a decreasing rate in the first two or three inches, after which the flow attains a steady rate. For practical purposes, the average time for films of various capacities to traverse given distances is directly proportional to the distance traversed. A direct proportion between travel time and D potency was established This may be due to the fact that the flow is turbulent, causing an interchange of substances in the surface zone within which



Courtesy of the Hanovia Co.

FIGURE 158. Diagram of Hanovia Milk Irradiator.

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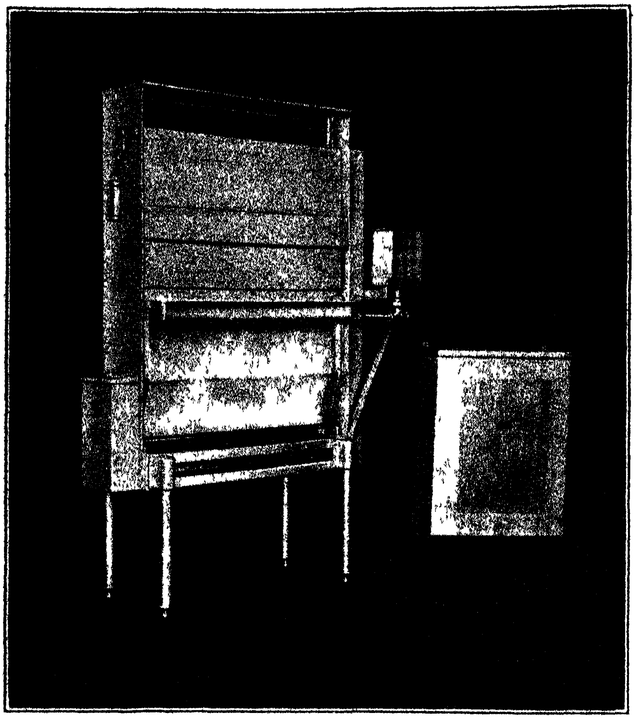
[170] Beck, H. H., and Weckel, K. G., *Ind Eng. Chem.*, **28**, 1251 (1936).

[171] Beck, H. H., and Weckel, K. G., *Ind. Eng. Chem. (Anal. Ed.)*, **8**, 258 (1936). See also Beck, H. H., Jackson, H. C., and Weckel, K. G., *Ind. Eng. Chem.*, **30**, 632 (1938).

the absorption and reaction occurs. The thickness of the film in thousandths of an inch may be calculated from the capacity X by the expression: $T = 1.79\ X^{0.875}$. The average velocity in inches per second is given by $0.349\ X^{0.625}$. The potency has a parabolic relation to the amount of active radiation applied, and the film capacity-potency relation is hyperbolic. O'Brien, McEwen and Morgareidge[172] calculate that if all the provitamin in whole milk could be converted, the potency would be 2.0 I.U. per gram. Using arc inputs of 300 joules per gram, they obtained 1.65 I.U. per gram.



Courtesy Hanovia Chemical and Manufacturing Co.

FIGURE 159. Hanovia Milk Irradiator.

During the commercial irradiation of milk, the destruction of vitamin A is insignificant or not measurable,[173] but vitamin C may be slightly affected, although to an extent less than the usual variations in non-irradiated milk.[174]

The question has often been raised as to whether better prophylactic results can be obtained by irradiation than by the administration of the vitamin in some form. Apparently, there is little if any difference, but since radiation therapy is less readily available the latter must usually be relied upon in practice.[175]

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[172] O'Brien, B., McEwen, H. D., and Morgareidge, K., *Ind. Eng. Chem*, **30**, 839 (1938).

[173] Supplee, G. C., and Dow, O. D., *J. Biol. Chem.*, **75**, 227 (1927); *Am. J. Diseases of Children*, **41**, 1353 (1931); Cannon, H. J., and Hixson, O. F, *Ind Eng Chem*, **28**, 1009 (1936)

[174] See also Schoenleber, F. C, Steenbock, H., and Baumann, C. A., *Wis. Agr. Expt. Sta. Bull. 435*, 66 (1936); *Chem. Abs.*, **32**, 2986 (1938).

[175] British Med. Research Council, *J. Soc. Chem Ind*, **48**, 279 (1929), Gorter, E., and Soer, J. J., *Nederland. Tijdschr. Geneesk.*, **74**, **II**, 4310 (1930); Machti, A., *Pediatria Rivista*, **37**, 1175 (1929); Shohl, A. T., and Bing, F. C., *Am J. Physiol.*, **86**, 633 (1928); von Noel, L., and Dannmeyer, F., *Strahlentherapie*, **32**, 769 (1929); *Chem. Abs.*, **24**, 4808 (1930); Blunt, K., and Cowen, R., "Ultraviolet Light and Vitamin D. in Nutrition," Univ. of Chicago Press, 1930.

It has been demonstrated by Hume, Lucas and Smith[176] that vitamin D from irradiated cholesterol can be absorbed from a small area of undamaged skin in amounts sufficient to supply the needs of the rat and rabbit. Similar results have been recorded by Astrowe and Morgen,[177] by Fodor,[178] by Amrhein,[179] and by Helmer and Jansen.[180]

The demonstration that the vitamin is absorbed from the skin and the assumption that it may exert a beneficial effect on the skin have prompted many proposals for its local application. Lorenz and Wodlinger[181] incorporate an irradiated sterol in toilet soap during crutching or milling. Cholesterol, phytosterol, zymosterol, etc. were irradiated with x-rays, infrared rays or cathode rays. Wearham[182] adds ergosterol to the soap or to the fats to be saponified and irradiates the mixture.

In a cosmetic skin cream, Goodall[183] proposed the use of cottonseed oil which had been treated with ultraviolet rays along with a mineral oil and a waxy substance. Apparatus for irradiating wool fat or wool-fat alcohols for use in cosmetic creams has been described.[184]

Autolyzed yeast, mixed with organic solvents and irradiated, has been proposed for use in treating the skin.[185]

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[176] Hume, F. M, Lucas, N. S., and Smith, H. H., *Biochem. J.*, **21**, 362 (1927).

[177] Astrowe, P. S., and Morgen, R. A., *Am. J. Diseases Children*, **49**, 912 (1935); *Chem. Abs.*, **29**, 5158 (1935).

[178] Fodor, M. E., *Z. Vitaminforschung*, **3**, 241 (1934); *Chem. Abs.*, **29**, 5487 (1935).

[179] Amrhein, F. J., *J. Am. Pharm. Assoc.*, **22**, 182 (1934); *Chem Abs.*, **28**, 5505 (1934). For a review, see Schuler, R., *Drug and Cosmetic Industry*, **38**, 485 (1936).

[180] Helmer, A. C., and Jansen, C. H., *Studies Inst. Divi Thomae*, **1**, 83, 99 (1937).

[181] Lorenz, A. J., and Wodlinger. M. H., British P. 403,083, June 10, 1932; *Chem. Abs.*, **28**, 3261 (1934); French P. 742,181, March 1, 1933; *Chem. Abs.*, **27**, 3632 (1933); Lorenz, A. J., U. S. P. 2,060,228 (to Lever Bros.); *Chem. Abs*, **31**, 566 (1937).

[182] Wearham, J, British P. 403,650, Dec. 20, 1933, *Chem. Abs.*, **28**, 3261 (1934).

[183] Goodall, F. E., U. S P. 1,636,814, May 3, 1927; *Chem. Abs.*, **21**, 2171 (1927).

[184] Leo-Werke, German P. 622,373, Nov. 27, 1935; Austrian P. 137,455, May 11, 1934.

[185] Baeder Illatszergyár, R. T., Hungarian P. 114,585; July 1, 1936; *Chem. Abs.*, **30**, 7284 (1936)

Chapter 41

Ultraviolet Light and Other Vitamins

Although some have suggested that vitamins other than D may also be produced by the irradiation of precursors,[1] no evidence exists for such processes. Suggestions have been made repeatedly that the formation of vitamins, particularly A and C, is in some manner related to the processes of photosynthesis.[2]

Too little is yet known of the mechanism of the photosynthetic formation of carbohydrates for definite statements to be made regarding a possible participation of either vitamin A or C, but the evidence as yet available is not very strongly in favor of this viewpoint.

Measurements of the ultraviolet absorption spectra of vitamin concentrates have significantly aided in the isolation and identification of the vitamins, and studies of the destruction of the purified compounds during irradiation have led to definite results.

Vitamin C. Reyher and Meller[3] observed that a prolonged irradiation of milk with exclusion of air causes some loss in its antiscorbutic properties. When irradiated in an open vessel under conditions in which ozone may be formed, there is a complete destruction of the vitamin. The loss which occurs in the practical irradiation of milk for the production of vitamin D is not important.[4] Booth and Kon[5] observed that milk which originally gave the vitamin C test based upon the reduction of the indophenol reagent, failed to do so after direct exposure to sunlight. Treatment for an hour with hydrogen sulfide restored 90 per cent of the original reducing value. The non-restorable loss increased with the duration of the exposure, so that after six hours only 50 per cent could be restored by the hydrogen sulfide treatment. The destruction follows a unimolecular course. The destruction in milk may be photosensitized by lactoflavin.[6] Indeed, Hopkins maintains that in pure buffered solutions at pH 7.4, ascorbic acid is stable in sunlight, although it is rapidly oxidized in the presence of small amounts of lactoflavin.[7] Ultraviolet light, however, causes a decomposition of *l*-ascorbic acid, even in the absence of oxygen.[8] This change is also accelerated by lactoflavin, but is retarded by acid. Dehydroascorbic acid could not be detected in the products formed. This oxidized form is not affected by irradiation.

Milanesi[9] failed in attempts to increase the amount of this vitamin in oats by irradiation and concluded that it was destroyed or altered by the treatment.

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[1] Bowden, F P., and Snow, C. P., *Nature*, **129**, 720 (1932)

[2] Heller, V. G., and St. Julian, R. R., *J Nutrition*, **4**, 227 (1931); *Chem. Abs.*, **25**, 5915 (1931); Heller, V. G., *J. Biol. Chem.*, **76**, 499 (1928); Crist, J W., and Dye, M., *Ibid.*, **91**, 127 (1931); Smith, L. L. W., and Morgan, A. F., *Ibid.*, **101**, 43 (1933).

[3] Reyher, P., and Meller, B., *Klin Wochschr.*, **5**, 2341 (1926); *Chem Abs*, **21**, 2149 (1927).

[4] Hottinger, A., *Klin. Wochschr*, **6**, 1793 (1927); *Chem Abs.*, **22**, 798 (1928); Supplee, G. C., and Dow, O. D., *Am. J. Diseases of Children*, **41**, 1353 (1931).

[5] Booth, R. G., and Kon, S. K., *Nature*, **134**, 936 (1934); Kon, S. K., and Watson, M. B., *Biochem. J.*, **30**, 2273 (1936).

[6] Hand, D. B, Guthrie, E. S., and Sharp, P F., *Science*, **87**, 439 (1938).

[7] Hopkins, F. G., *Compt rend. trav. lab. Carlsberg, Sér. chim.*, **22**, 226 (1938); *Chem. Abs.*, **32**, 6265 (1938).

[8] Kellie, A. E., and Zilva, S. S., *Biochem J.*, **32**, 1561 (1938).

[9] Milanesi, E., *Boll. soc. ital. biol. sper.*, **3**, 240 (1928); *Chem. Abs.*, **22**, 3911 (1928).

Cultrera [10] found the reducing factor of lemon juice to be destroyed by Wood's light. According to v. Euler and Klussmann,[11] the optical activity of hexuronic acid decreases when it is kept in a current of oxygen under ultraviolet rays. Ascorbic acid is now known to have an absorption maximum at 2600A in water and at 2630 to 2650A in alcohol.[12]

Eggleton and Harris [13] conclude that light is unnecessary for the natural synthesis of this vitamin. Irradiation of infant food did not increase its content of ascorbic acid. Mercury-arc irradiation of cabbage in which the vitamin had been destroyed by heat gave but a doubtful regeneration. Irradiation has no curative action on scorbutic animals.[14] Heller [15] has claimed that the formation of vitamin C (and also A), although it occurs during the germination and early growth of seedlings in darkness, is accelerated by exposure to light. Similar observations have since been reported by Matsuoka [16] and by Lee and Read.[17] Virtanen and Eerola [18] tend to ascribe such results to an effect of temperature rather than light, at least in the case of the pea.

It has been claimed that a brief irradiation by ultraviolet light of the skin of a guinea pig increases its ascorbic acid content, although a longer one (25 minutes) decreases it.[19]

The claim of Rygh [20] that vitamin C could be obtained by the irradiation of narcotine derivatives has since been refuted.[21] It appears to have been based upon unsuitable biological testing of the irradiation product.

Several observers have noted irradiation, particularly with visible light in the presence of a photosensitizer such as methylene blue, to lower the redox potential of ascorbic acid.[22] It has been proposed to take advantage of this property in a method for the assay of ascorbic acid in tissues.[23] Cornbleet [24] finds irradiation of skin to lower its ascorbic acid content. Pigmented skin has more ascorbic acid than fair skin. Buruianâ believes it possible to determine the vitamin C content of milk by comparing the reduction of iodine before and after the exposure of the milk to sunlight.[25]

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[10] Cultrera, R., *Ind ital. conserve aliment*, **9,** 9 (1934); *Chem. Abs*, **28,** 3763 (1934).

[11] v. Euler, H., and Klussmann, E., *Svensk Kem. Tid.*, **44,** 290 (1932); *Chem. Abs.*, **27,** 4566 (1933)

[12] Herbert, R. W, and Hirst, E. L., *Nature*, **130,** 205 (1932), *Biochem J.*, **29,** 1881 (1935); Bowden, F. P, and Snow, C. P., *Nature*, **129,** 720 (1932); Karrer, P., Schwarzenbach, G., and Schopp, K., *Helv. Chim. Acta*, **16,** 181 (1933), Robertson, E. B, *J. Soc Chem Ind*, **53,** 277 (1934); Plaut, F., Bulow, M., and Pruckner, F., *Z. physiol Chem*, **234,** 131 (1935).

[13] Eggleton, P., and Harris, L. J., *Brit Med J*, **II,** 989 (1925), *Chem. Abs.*, **20,** 1651 (1926).

[14] Holtz, P., and Wöllpert, K, [*Arch. Exptl. Path. Pharmakol.*, **182,** 164 (1936)] believed it to cause some delay in the onset of scurvy

[15] Heller, V. G, *J. Biol Chem*, **76,** 499 (1928).

[16] Matsuoka, T., *Mem. Coll. Agr. Kyoto Imp. Univ.*, **24,** 37 (1932); **35,** 93 (1935); *Chem. Abs.*, **27,** 2180 (1933); **30,** 139 (1936); *J. Agr. Chem. Soc. Japan*, **9,** 81 (1933); **12,** 1203 (1936), *Chem. Abs.*, **31,** 3103 (1937).

[17] Lee, Wei-Yung, and Read, B. E., *J. Chinese Chem. Soc.*, **4,** 208 (1936); *Chem. Abs*, **31,** 430 (1937). See also Tsuge, H., and Kurihara, K, *Sei-i-kai Med. J*, **56,** No. 6, 894 (1937); *Chem Abs*, **31,** 8610 (1937); Randoin, L., Giroud, A., and Ratsimamanga, R, *Compt rend. soc. biol.*, **126,** 1068 (1937), *Chem. Abs*, **32,** 2570 (1938).

[18] Virtanen, A. I., and Eerola, L. V, *Suomen Kemistilehti*, **9B,** 13 (1936); *Chem. Abs*, **31,** 2254 (1937). See, however, Veselkin, N. V., Lyubimenko, V. N., Bulgakosa, S P., Tichalskaya, V. V., and Engel, P. S., *Isv. Nauch. Inst. Lesgafta*, **17,** 389, 405 (1934); *Chem Abs.*, **31,** 6696 (1937).

[19] Castellini, P., *Giorn. ital. dermatol. sifilol.*, **77,** 967 (1936); *Chem. Abs.*, **32,** 226 (1938).

[20] Rygh, O., Rygh, A., and Laland, P., *Z. physiol. Chem.*, **204,** 105; **211,** 275 (1932).

[21] Westin, G, *Z. Vitaminforsch.*, **2,** 1 (1933); *Chem. Abs.*, **27,** 4560 (1933), Shimada, J., *J. Biochem. Japan*, **17,** 395 (1933); *Chem. Abs.*, **27,** 5103 (1933).

[22] Viale, G, *Rev. sudamer. endocrinol. immunol. quimio-terap*, **17,** 547 (1934); *Chem. Abs.*, **28,** 6794 (1934); Lund, H, and Lieck, H., *Skand. Arch Physiol.*, **74,** 269 (1936); Martini, E., *Biochim. terap sper.*, **20,** 505 (1933); *Chem. Abs.*, **28,** 3456 (1934).

[23] Martini, E., and Bonsignore, A., *Boll. soc. ital. biol. sper.*, **9,** 388 (1934); *Chem. Abs.*, **28,** 6460 (1934), Bonsignore, A., *Boll. soc. ital. biol. sper.*, **10,** 62 (1935); *Chem. Abs*, **29,** 3385 (1935).

[24] Cornbleet, T., *Arch. Dermatol. Syphilol.*, **35,** 471 (1937); *Chem. Abs.*, **31,** 5412 (1937).

[25] Buruianâ, L., *Biochem. J.*, **31,** 1452 (1937).

Vitamins of the B Group. During the early difficult period when the multiplicity of the water-soluble vitamins other than ascorbic acid was being investigated and when but two such products were definitely recognized, attempts were made, in anticipation of any knowledge of their structure or absorption spectra, to differentially destroy one but not the other by the aid of ultraviolet light. This treatment was intended to be applied to yeast used in experimental diets for the production of deficiencies, the growth factor other than B_1 being the more susceptible.[26] Kennedy and Palmer [27] doubted that such methods could be relied upon, since both factors could be destroyed, but with varying ease. Hogan and Hunter showed that autoclaving had the opposite effect, destroying the antineuritic factor more rapidly than the growth factor. Hogan and Richardson [28] claimed to have attained satisfactory results in the destruction of the antidermatitis factor by mercury-arc irradiation. Guerrant and Salmon [29] found the destruction of the growth-promoting factor to proceed more rapidly when the irradiation was applied to an alkaline solution. After the later recognition of the flavins as growth-promoting factors, Hogan and Richardson [30] reinvestigated the matter and concluded that in irradiation of the diets both the flavins and an unidentified factor essential for the prevention of dermatitis are destroyed. It has since been shown by others that the rat antidermatitis factor is pyridoxine [2-methyl-3-hydroxy-4,5-di-(hydroxymethyl)-pyridine]. In the determination of its structure, ultraviolet absorption spectra gave important information. Nicotinic acid, the antipellagra factor, has an absorption maximum at about 2600A.[31]

Contrary to these observations, Halliday and Evans [32] state that none of the factors present in brewers' yeast extract was destroyed by ten hours of irradiation. Doubtless this result is to be ascribed to the presence of substances in the extracts which act as internal filters. It is now known that B_1 (thiamine), the flavins and nicotinic acid can be destroyed when solutions of the pure substances are irradiated by ultraviolet light (visible light in the case of the flavins). Gyorgy [33] finds a pellagra-preventing factor to be destroyed by visible light, at the same time changing from yellow to brown.

Before the chemical purification of B_1 concentrates had advanced to a stage in which sulfur was recognized as a constituent of the compound, attempts were made to prepare the vitamin from various precursors. Heyroth and Loofbourow [34] called attention to the resemblance of the ultraviolet absorption spectra of highly purified concentrates to the spectra of purines and pyrimidines and noted that irradiation of the latter with ultraviolet light from which the shorter wave-lengths had been excluded seemed to increase the resemblance. They showed, however,[35] that irradiated nucleic acids and irradiated uracil lacked antineuritic and growth-promoting properties. Guha [36] claimed to have been successful in producing the antineuritic vitamin by the irradiation of adenine. Other workers confirmed the observations of Heyroth that the vitamin cannot be produced by the irradiation of a simple purine or pyrimidine[37] and Guha and Chakravorty[38] later admitted that irradiated adenine does not cure avian polyneuritis, although they still believed it to have growth-promoting properties. This Schultz and Laquer suggest may have been due to a contamination of the adenine used by one of the growth-promoting vitamins of the B group.

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[26] Hogan, A. G., and Hunter, J. E., *J. Biol. Chem.*, **78**, 433 (1928).

[27] Kennedy, C., and Palmer, L. S., *J. Biol. Chem.*, **83**, 493 (1929)

[28] Hogan, A. G., and Richardson, L. R., *Mo. Agr. Exp. Sta Research Bull.*, *178*, 3 (1932)

[29] Guerrant, N. B., and Salmon, W. D., *J. Biol. Chem.*, **89**, 199 (1930).

[30] Hogan, A. G., and Richardson, L. R., *Nature*, **136**, 186 (1935); *Science*, 83, 17 (1936); *Mo. Agr. Exp. Sta., Bull. 340*, 26 (1934).

[31] Compare the absorption of a growth-factor called B_2 by Karrer, P., and von Euler, H., *Arch. Kemi, Mineral Geol.*, **11B**, No. 16 (1933); *Chem. Abs.*, **27**, 5101 (1933).

[32] Halliday, N., and Evans, H. M., *J. Biol. Chem.*, **118**, 255 (1937).

[33] György, P., *Biochem. J.*, **29**, 767 (1935)

[34] Heyroth, F. F., and Loofbourow, J. R., *Bull Basic Science Research*, **3**, *237* (1931).

[35] Heyroth, F. F., and Loofbourow, J. R., *Nature*, **131**, 92 (1933); *Bull. Basic Science Research*, **4**, 119 (1932).

[36] Guha, B. C., *Nature*, **130**, 741 (1932) Bonner, J., and Greene, J., [*Botan Gaz.*, **100**, 226 (1938); *Chem. Abs.*, **32**, 9185 (1938)] believe the thiamin content of pea plants increases in light.

Heyroth and Loofbourow[39] later studied samples of crystalline thiamine (B_1) as well as concentrates of varying degrees of purity. It was shown that pure thiamine had absorption maxima at about 2650A and 2350A. Ultraviolet irradiation destroys the physiological activity and reduces the extinction coefficients.[40] An oxidation product, thiochrome, which has an intense fluorescence employed for assay purposes, is rapidly destroyed by ultraviolet light.[41]

Absorption studies and observations of the destructive effects of irradiation with visible light have played an important part in the development of our knowledge of the flavins as growth-promoting vitamins. The brilliant green fluorescence of these materials led to their discovery and guided their isolation. That the flavins in aqueous alkaline solution could be photochemically inactivated by visible light was shown in one of the first papers dealing with these substances.[42]

During this process there was produced a colored substance soluble in chloroform, which came to be known as a lumiflavin or lumichrome.[43]

It was shown by Kuhn and Wagner-Jauregg[44] that the photolysis consists in the splitting off of an oxygen-rich, nitrogen-free group of atoms:

$$\underset{\textit{Lactoflavin}}{C_{17}H_{20}N_4O_6} - C_4H_8O_4 \rightarrow \underset{\textit{Lumilactoflavin}}{C_{13}H_{12}N_4O_2}$$

Other flavins, such as uroflavin, maltoflavin and hepatoflavin were shown to undergo a similar photolysis,[45] which involves the loss of a sugar-like side-chain. In searching for analogies for this behavior, Kuhn and Bär[46] showed that when 2-tetraoxybutylquinoxaline is irradiated in alkaline solution, the tetraoxybutyl residue held on a carbon atom is replaced by an atom of hydrogen with the formation of the chloroform-soluble quinoxaline. In this case, however, the original compound was colorless so that it was necessary to employ ultraviolet light.

Similarly, Ohle[47] found the closely related 3-tetraoxybutyl-2-oxyquinoxaline loses not four but three carbon atoms as glycerin and yields 2-oxyquinoxaline-3-aldehyde. Irradiation of an alkaline solution of pentahydroxyamyl-benzimidazole gives a small amount of benzimidazole; the main photochemical product was not identified.[48]

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[37] Schultz, F., and Laquer, F., *Z physiol Chem.*, **219**, 158 (1933); Sure, B., *Biochem. J.*, **27**, 2043 (1933); Yamamoto, R., and Yamagishi, T, *J. Agr Chem. Soc. Japan*, **9**, 749 (1933); *Chem. Abs.*, **27**, 5381 (1933) It was early shown that irradiation of a polyneuritic animal has no favorable effects Krizenecky, J., *Arch. ges. Physiol, (Pflüger's)*, **204**, 407 (1924); **211**, 663 (1926); *Chem. Abs.*, **20**, 1437 (1926).

[38] Guha, B C., and Chakravorty, P. N., *Nature*, **132**, 447 (1933), *J Indian Chem. Soc.*, **11**, 195 (1934); *Chem. Abs.*, **28**, 5503 (1934).

[39] Heyroth, F. F., and Loofbourow, J. R., *Bull Basic Sci. Research*, **4**, 35 (1932); *Nature*, **134**, 461 (1934); *Biochem J.*, **30**, 651 (1936), see also Peters, R. A., and Philpot, J., *Proc. Roy. Soc.*, **B113**, 48 (1931); Holiday, E R., *Biochem. J.*, **29**, 719 (1935); Wintersteiner, O., Williams, R R., and Ruehle, A. E., *J. Am. Chem. Soc.*, **57**, 517 (1935).

[40] Heyroth, F. F., and Loofbourow, J. R., *J. Am. Chem. Soc.*, **56**, 2010 (1934); Kakefuda, H., *Fukuoka Acta Med.*, **27**, 99 (1934); *Chem Abs.*, **29**, 6278 (1935).

[41] Otto, H., and Rühmekorb, F., *Klin. Wochschr.*, **17**, 1246 (1938); *Chem. Abs.*, **32**, 9133 (1938).

[42] Kuhn, R., György, P., and Wagner-Jauregg, T., *Ber.*, **66**, 317 (1933).

[43] Ellinger, P., and Koschara, W., *Ber.*, **66**, 808, 1411 (1933).

[44] Kuhn, R., and Wagner-Jauregg, T., *Ber.*, **66**, 1577 (1933); Kuhn, R., Rudy, H, and Wagner-Jauregg, T., *Ber.*, **66**, 1950 (1933).

[45] Stern, K. G., *Nature*, **133**, 178 (1934); Koschara, W., *Z. physiol. Chem.*, **229**, 103 (1934); Bierry, H., and Gouzon, B., *Compt. rend.*, **200**, 2116 (1935); *Chem. Abs.*, **29**, 6911 (1935).

[46] Kuhn, R., and Bar, F., *Ber.*, **67**, 898 (1934).

[47] Ohle, H., *Ber.*, **67**, 155 (1934).

It was later shown by Kuhn and Rudy [49] that during the loss of the sugar-like side-chain in the photolysis of the flavin an alkyl group becomes attached to a nitrogen atom. After much further work, it has been shown that lumilactoflavin is 6,7,9-trimethylisoalloxazine.[50]

In work on the synthesis of substances similar to lactoflavin, Karrer, Schlittler, Pfaehler and Benz [51] noted that their synthetic 9-(betahydroxyethyl) isoalloxazine when irradiated by sunlight in neutral solution gave 9-methylisoalloxazine. In alkaline solution, irradiation gave alloxazine and its 9-methyl derivative. Lumichrome was also obtained from ovoflavin *c* [52] and lactoflavin.[53] Karrer attributes the light-sensitivity of lactoflavin to the presence of a single β- hydroxyl group in the sugar-like side-chain.

When a synthetic branched-chain flavin, 9-(2′,3′-dihydroxy-1′-isopropyl)-isolloxazine, is illuminated in water or methanol solution, it slowly breaks down yielding some alloxazine, the decomposition appearing to start at the hydroxyl in the 2′ position of the side-chain. In alkaline solution, however, easily soluble colorless compounds were formed by the action of light, and no alloxazine could be detected.[54] The decomposition by sunlight of a flavin containing a tertiary hydroxyl group, such as 9-(2′-hydroxy-2′-methyl-1′-propyl)isoalloxazine, however, shows [55] that it is not necessary that dehydrogenation occur at the 2′ position of the hydroxy side-chain. The rate of decomposition is much slower with this compound than with flavins containing a primary or a secondary group. As with the other flavins, the photolysis proceeds more rapidly in aqueous methanol than in water.

Subsequently, Karrer, Köbner, Salomon and Zehender [56] drew more clearly the distinction between the decomposition of lactoflavin to lumichrome (that is, alloxazine) derivatives which occurs in neutral solutions and that of 9-γ-hydroxypropyl isoalloxazine, which fails to react in neutral solutions but is rapidly decomposed to alloxazine in alkaline solutions. The former reaction is said to be a dehydration commencing by oxidation at the β-CHOHCO.[57]

Flavins may exert a photosensitizing action upon ascorbic acid since its oxidation potential falls in light more rapidly in their presence than in their absence.[58] The brilliant fluorescence of the flavins has been employed in this essay,[59] and practical rapid methods for the application of the Fluoray lamp to the assay of flavins in milk have been given by Whitnah, Kunerth and Kramer [60] and by Supplee, Ansbacher, Flanigan and Hanford.[61]

[48] Kuhn, R, and Bar, F, *Ber*, **67B**, 898 (1934); Kuhn and Weygand, F., *Ber.*, **67B**, 1939 (1934).

[49] Kuhn, R., and Rudy, H., *Ber*, **67**, 1298 (1934).

[50] Kuhn, R., Reinemund, K, and Weygand, F., *Ber*, **67**, 1460 (1934); Kuhn, R. and Rudy, H. [*Ber.*, **67B**, 1936 (1934)] state that lumichrome, similarly formed by irradiation in neutral or acid solutions is 6,7-dimethylalloxazine.

[51] Karrer, P., Schlittler, E, Pfaehler, K., and Benz, F., *Helv Chim Acta*, **17**, 1516 (1934).

[52] Karrer, P., and Schöpp, K., *Helv. Chim. Acta*, **17**, 1557 (1934).

[53] Karrer, P., Salomon, H., Schöpp, K., Schlittler, E., and Fritzsche, H., *Helv. Chim. Acta*, **17**, 1010 (1934).

[54] Karrer, P., and Meerwein, H., *Helv Chim. Acta*, **18**, 480 (1935).

[55] Karrer, P., and Meerwein, H., *Helv. Chim Acta*, **18**, 1126 (1935).

[56] Karrer, P., Köbner, T, Salomon, H, and Zehender, F., *Helv Chim Acta*, **18**, 266 (1935).

[57] For further details concerning the structure of related compounds as affecting the photolysis, see, Karrer, P., and Musante, C., *Helv Chim Acta*, **18**, 1134 (1935), Karrer, P., Köbner, T., and Zehender, F., *Ibid.*, **19**, 261 (1936); Karrer, P., and Naef, R., *Ibid*, **19**, 1029 (1936).

[58] Martini, E., *Boll. soc ital. soc. biol. sper.*, **9**, 1235 (1934); *Chem Abs.*, **29**, 2580 (1935); Süllmann, H., *Klin. Wochschr.*, **17**, 1157 (1938); *Chem Abs.*, **32**, 8273 (1938)

[59] Josephy, B., *Acta Brevia Neerland. Physiol. Pharmacol, Microbiol*, **4**, 46 (1934); *Chem. Abs.*, **29**, 3362 (1935); Cohen, F. H., *Acta Brevia Neerland Physiol Pharmacol, Microbiol.*, **4**, 46 (1934); **5**, 18 (1935); *Chem. Abs.*, **29**, 4044, 4790, 5482 (1935); *Rec. trav. chim.*, **54**, 133 (1935); Bierry, H., and Gouzon, B., *Compt. rend soc. biol*, **119**, 101 (1935); *Chem. Abs*, **29**, 5133 (1935); Karrer, P., and Fritzsche, H, *Helv. Chim. Acta*, **18**, 911 (1935); van Eekelen, M., and Emmerie, A., *Acta Brevia Neerland. Physiol. Pharmacol Microbiol*, **5**, 77 (1935); Weisberg, S. M., and Levin, I., *Ind. Eng. Chem. (Anal. Ed.)*, **9**, 523 (1937).

[60] Whitnah, C. H., Kunerth, B. L., and Kramer, M. M., *J Am Chem Soc.*, **59**, 1153 (1937).

[61] Supplee, G. C., Ansbacher, S., Flanigan, G. E., and Hanford, Z. M., *J. Dairy Sci.*, **19**, 215 (1936).

It must also be noted that the methods of irradiation which proved so helpful in the study of the constitution of the flavins had in fact been based upon similar previous observations of the behavior of a yellow oxidation enzyme obtained from yeast by Warburg and Christian,[62] and which contains a flavin prosthetically bound to a protein. Observations by Theorell[63] show that so long as the active group (flavin phosphate) is combined with protein, it is unchanged by light, but when liberated in alkaline solution it behaves like lactoflavin. The destruction of the flavin or its ester proceeds more rapidly in the presence of oxygen than in its absence, but more rapidly in air than in pure oxygen. In an argon atmosphere, deuteroleucoflavin phosphate is first formed, and on continued irradiation in the absence of oxygen slowly splits to 6,7-dimethylalloxazine; on the admission of air, however, the unchanged leuco- compound is at once oxidized to deuteroflavin phosphate, which is rapidly split to dimethylalloxazine by light. Therefore, in the presence of air the deuterocompounds are not formed. In a strongly alkaline medium, the deuteroflavin is changed quantitatively to lumiflavin without the formation of dimethylalloxazine.

Vitamin A. Absorption spectrum studies have played a large part in the study of the constitution of vitamin A, as well as that of carotene which may replace it in the diet, being converted into the vitamin in the liver.[64]

Morton and Heilbron[65] showed that vitamin A concentrates exhibit a prominent absorption band at 3285A, the intensity of which accords with the potency as determined by the depth of a blue color produced by antimony trichloride. In some fish oils, however, as in dogfish oil, the characteristic absorption band may be masked by absorption bands due to other substances. General confirmation of the absorption of the vitamin at 3280A was given by Drummond and Morton.[66] Evidence has been brought forward recently for the existence in the livers of certain fresh-water fishes of a second vitamin A, A_2, with an absorption maximum displaced to 3450-3500A.[67]

The Hilger Vitameter has been introduced to facilitate the assay of vitamin A by measuring the 3280A band.[68] In the development of absorption assay methods account must be taken of the absorption of carotene since that substance is physiologically equivalent to the vitamin. Its absorption spectrum is different,[69] lacking the band at 3280A. It has bands between 3300 and 3400A and between 2630 and 2950A.[70] The discovery of the conversion of carotene into vitamin A in the liver has been followed by spectrographic methods. Capper[71] showed that the liver oil of rats deficient in vitamin A lacked its characteristic 3280A band and that this was present in the liver oil of rats which had been cured by the administration of carotene. Basu[72] suggested that this change can occur only in animals receiving ultraviolet radiations. Bowden and Snow[73] believed that irradiation of β-carotene in cyclohexane produces a change in the absorption spectrum indicative of the production of vitamin A, but Dann[74] believes that this is precluded by the fact that the vitamin is more rapidly destroyed than is carotene by the 2650A line.

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[62] Warburg, O., and Christian, W., *Naturwiss.*, **20,** 980 (1932); *Biochem. Z.*, **258,** 496 (1933); British P. 430,571, June 17, 1935; *Chem. Abs.*, **29,** 7362 (1935).

[63] Theorell. H., *Biochem. Z.*, **279,** 186 (1935).

[64] Morton, R A, "Applications of Absorption Spectra to the Study of Vitamins and Hormones," London, A Hilger, Ltd; Chevallier, A, *Bull. soc. chim biol.*, **17,** 530 (1935); Rosenthal, J., and Weltner, M. *Biochem. J*, **29,** 1036 (1935), De, N. K., *Indian J. Med Research*, **22,** 509 (1935).

[65] Morton, R. A, and Heilbron, I. M, *Nature*, **122,** 10 (1928); *Biochem J*, **22,** 987 (1928).

[66] Drummond, J. C., and Morton, R. A., *Biochem. J.*, **23,** 785 (1929). Morton, R. A., Heilbron, I M, and Spring, F S., [*Biochem J.*, **24,** 136 (1930)] answer certain objections raised by Rosenheim, O, and Webster, T A., *Ibid.*, **23,** 633 (1929). See also Woodrow, J. W., and Cunningham, H. L., *Phys. Rev.*, **35,** 125 (1930); Woodrow, J. W., and Philipson, J. B., *Proc. Iowa Acad. Sci*, **37,** 310 (1930); Coward, K. H. Dyer, F. J., and Morton, R. A., *Biochem J*, **26,** 1593 (1932); Chevallier, A, and Chabre, P., *Biochem J.*, **27,** 298 (1933); Josephy, B., *Acta Brevia Neerland. Physiol. Pharmakol. Microbiol.*, **3,** 133 (1933), *Chem. Abs.*, **28,** 2467 (1934); Crews, S K., and Cox, S. J., *Analyst*, **59,** 85 (1934); *Chem Abs.*, **28,** 2756 (1934).

[67] Gillam, A. E., Heilbron, I. M., Lederer, E., and Rosanova, V, *Nature*, **140,** 233 (1937); Edisbury, J. R., Morton, R. A., and Simpkins, G. W., *Ibid.*, **140,** 234 (1937); Lederer, E., and Rathmann, F. H., *Biochem. J.*, **32,** 1252 (1938) Compare Chevallier, A, and Choron, Y., [*Compt. rend.*, soc. biol., **127,** 1443 (1938); *Chem. Abs*, **32,** 6298 (1938)] who distinguish hemo- and hepato-forms of vitamin A.

[68] French P 760,676, Feb. 28, 1934, to Adam Hilger Ltd; *Chem. Abs*, **28,** 4180 (1934); British P. 416,423, Sept 19, 1934; Twyman, F, and Follet, D H, U. S P. 2,065,953, Dec. 29, 1936, to Adam Hilger Ltd.; *Chem. Abs.*, **31,** 911 (1937); Irish, F W., *J. Assoc., Off. Agr Chem.*, **19,** 244 (1936); Wilkie, J. B., *Ibid.*, **20,** 208 (1937); Notevert, O., *Biochem. J.*, **29,** 1227 (1935); Baumann, C. A, and Steenbock, H., *J. Biol Chem*, **101,** 547 (1933); Baumann, C. A., Steenbock, H., Beeson, W. M., and Rupel, I. W, *Ibid.*, **105,** 167 (1934); Shrum, G. H., and How, T. G, *Can. J. Research*, **13A,** 93 (1935); McFarlane, W., and Rudolph, L., *Sci. Agr.*, **16,** 398 (1936); *Chem Abs*, **30,** 6405 (1936), Barthen, C. L., and Leonard, C. S., *J. Am Pharm. Assoc.*, **26,** 515 (1937); Holmes, A. D., Black, A., Eckler, C. R., Emmett, A. D., Heyl, F. W., Neilsen, C, and Quinn, E. J, *Ibid.*, **26,** 525 (1937); *Chem Abs.*, **31,** 6274 (1937); Nijveld. W. J., *Chem. Weekblad*, **34,** 379 (1937); *Chem. Abs.*, **31,** 7461 (1937); Leech, W. D., *Australian Chem. Inst J. and Proc.*, **5,** 155 (1938); *Chem. Abs.*, **32,** 6281 (1938); McFarlan, R L., and Reddie, J. W., U. S. P. 2,123,573, July 12, 1938; *Chem, Abs.*, **32,** 6510 (1938).

The extensive work on the assay of vitamin A by the spectrophotometric measurement of the intensities of colors produced on the addition of antimony trichloride lies beyond the scope of our present discussion.

The photochemical destruction of vitamin A has been very extensively studied. Earlier divergent findings were in large part due to the use of the antimony trichloride method, the results being somewhat masked by the effects of the several other chromogens which may accompany the vitamin in the oils and concentrates studied. It was first observed by Peacock[75] that the exposure of cod-liver oil to white light caused a loss of its fluorescence and of its ability to give the arsenic trichloride test then employed for the determination of the vitamin. The ability of the oil to promote growth in rats was lost. Confirmations were reported by Holmes and Pigott[76] and Titus, Hughes, Hinshaw and Fitch[77] stated that the irradiation of milk by a mercury arc caused a loss of some vitamin A. Zilva[78] reported that the irradiation of butter with ultraviolet light did not lead to the production of toxic substances as had been reported by Spinka.[79]

Willimot and Wokes[80] irradiated cod-liver oil in an open dish only three inches from a mercury arc, the temperature rising to 70° in 90 minutes. One third of the vitamin A, determined by the colorimetric method, was destroyed in the first hour and the whole of it in two hours. They also noted that after a few minutes of irradiation, a slow destruction of the vitamin continued for a long period. Morton and Heilbron[81] confirmed the results by noting the disappearance of the band at 3280A. Their absorption studies indicated that the first decomposition products of the vitamin might possess an absorption band in the region 2750 to 2850A. A very rich shark-liver oil was employed. Steenbock and Wirick[82] found the destruction of the vitamin in butter-fat to be proportional to the time of irradiation and inversely proportional to the thickness of the layer exposed. The process could be retarded by surrounding the fat with an inert gas.

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[69] Morton, R. A., and Heilbron, I. M , *Biochem J* , **24**, 870 (1930); Kawakami, K., *J. Agr Chem Soc. Japan*, **8**, 48 (1932); *Chem. Abs.*, **27**, 1661 (1933), Smith, J. H C., *J. Am. Chem. Soc.*, **58**, 247 (1936).

[70] See also Woodrow, J. W , and Philipson, J. B , *Proc Iowa Acad Sci* , **38**, 218 (1931); *Chem Abs.*, **27**, 2184 (1933); Winterstein, A., *Z. physiol. Chem.*, **215**, 51 (1933); von Euler, H., and Klussmann, E., *Arkiv Kemi, Mineral Geol.*, **11B**, No. 17 (1933); Miller, E. S., *Plant Physiol* , **9**, 179 (1934); *Bot. Gaz.*, **96**, 447 (1935); *Plant Physiol.*, **10**, 375 (1935); Karrer, P., and Solmssen, U., *Helv. Chim. Acta*, **18**, 25 (1935); Castle, D. C , Gillam, A. E., Heilbron, I. M , and Thompson, H. W., *Biochem. J.*, **28**, 1702 (1934). Carotene may be bleached by ultraviolet rays in treating cream for butter-making, according to H. E. Kistner, U. S. P. 2,119,461, May 31, 1938; *Chem. Abs.*, **32**, 5526 (1938).

[71] Capper, N. S., *Biochem J.*, **24**, 980 (1930).

[72] Basu, N. K., *Z. Vitaminforschung*, **3**, 254 (1934); *Chem Abs* , **29**, 5487 (1935).

[73] Bowden, F. P , and Snow, C. P., *Nature*, **129**, 720 (1932).

[74] Dann, W. J., *Biochem. J.*, **27**, 274 (1933); see also De, N. K., *Indian J. Med. Research*, **23**, 505 (1935).

[75] Peacock, P. R , *Lancet*, **II**, 328 (1926); *Science*, Oct. 15, **1926.**

[76] Holmes, A. D., and Pigott, M. G., *Boston Med. Surg J.*, **195**, 263 (1926).

[77] Titus, R. W., Hughes, J. S., Hinshaw, W. R., and Fitch, J. S., *Ind. Eng. Chem.*, **18**, 843 (1926)

[78] Zilva, S. S., *Biochem. Z.*, **155**, 333 (1925).

[79] Spinka, J., *Biochem. Z.*, **153**, 197 (1924).

[80] Willimot, S. G., and Wokes, F., *Pharm. J.*, **118**, 217 (1927); *Chem. Abs.*, **21**, 3220 (1927); *Lancet*, **II**, 8 (1927); *Chem. Abs.*, **22**, 257 (1928).

[81] Morton, R. A., and Heilbron, I. M., *Nature*, **122**, 10 (1928).

Norris[83] used both colorimetric and biological assays and conducted the irradiation of cod-liver oil in a rotating closed quartz cylinder under carbon dioxide, at a temperature not over 15°C. Preliminary work indicated an induction period of about two hours, although in subsequent experiments[84] this could be confirmed only for the biological assays. A plot of the reciprocals of the chromogen which with antimony trichloride gives absorption between 600 and 617 $m\mu$ against the time of exposure gave a straight line. The vitamin content reached zero after about four hours.

By colorimetric determinations, Evers[85] found little or no change in the first two hours, after which there was a slow change. Hawk[86] reported an actual increase in the antimony trichloride blue color during irradiation in air. Although denied by Drummond,[87] this observation was confirmed by Norris and Church[88] and by Heilbron, Gillam and Morton.[89]

Wave-lengths shorter than 3350 to 3400A are required for the destruction of the vitamin[90]

Chevallier[91] found carbon-arc irradiation of a hexane solution of an unsaponifiable vitamin A concentrate to produce a rapid destruction of the absorption band at 3280A. At the same time there was evidence from the absorption changes within the region 2900 to 3400A[92] of the production of new products which in turn were destroyed at different rates. One product formed may be an intermediate between vitamin A and β-ionone.[93] From the results of the use of filtered light of 3650A Chevallier and Dubouloz[94] calculated the quantum yield as 1/28, and noted that the decomposition follows a somewhat different course in slightly acid and in slightly alkaline ethanol. It is claimed that the formation of several decomposition products may be recognized by analysis of the spectrographic results.[95]

[82] Steenbock, H., and Wirick, A. M., *J Dairy Sci.*, **14**, 229 (1931), *Chem. Abs.*, **25**, 4030 (1931); Shrewsbury, C L., and Kraybill, H. R., *Science*, **75**, 86 (1932).

[83] Norris, R. J., *Bull Basic Sci. Research*, **3**, 89 (1931).

[84] Nabarro, D., and Hickman, J. O., found no change in thirty seconds, *Lancet*, **I**, 127 (1930).

[85] Evers, N., *Quart. J. Pharm.*, **2**, 556 (1929); *Brit Chem. Abs*, **A**, 1203 (1929).

[86] Hawk, P. B, *Science*, **69**, 200 (1929).

[87] Drummond, J. C, *J. Soc. Chem. Ind.*, **49**, 285T (1930).

[88] Norris, E R., and Church, A. E, *J. Biol. Chem.*, **89**, 421 (1930).

[89] Heilbron, I. M., Gillam, A. E., and Morton, R. A, *Biochem. J.*, **25**, 1352 (1931). Even the 3280A band increases during the first few minutes of irradiation, according to Boyle, E., *Nature*, **133**, 798 (1934); *Biochem. J.*, **28**, 573 (1934). See also Smith, E. L., Stern, B E., and Young, F. E., [*Nature*, **141**, 551 (1938)] who find that irradiation sometimes increases and sometimes decreases the absorption, which, however, returns to normal on standing in the dark. These changes may be due to *cis-trans* isomerization. Morton, R. A., *Nature*, **141**, 552 (1938).

[90] Norris, R. J. and Loofbourow, J. R., *Bull. Basic Sci. Research*, **4**, 113 (1932).

[91] Chevallier, A., *Compt. rend. soc. biol*, **112**, 1681 (1933); *Chem Abs.*, **27**, 3974 (1933).

[92] Chevallier, A., and Choron, Y., *Compt. rend. soc biol.*, **115**, 1297 (1934); *Chem. Abs.*, **28**, 4455 (1934).

[93] Chevallier, A, Choron, Y, and Guillot, J., *Compt. rend. soc. biol.*, **117**, 10 (1934); *Chem. Abs*, **29**, 201 (1935).

[94] Chevallier, A., and Dubouloz(P., *Bull. soc. chim. biol.*, **18**, 190, 703 (1936); *Brit. Chem. Abs.*, **A**, 1159 (1936).

[95] Chevallier, A., Dubouloz, P and Manuel, S., *Compt. rend soc. biol.*, **121**, 1415 (1936); Dubouloz, P., *J. chim. phys.* **33**, 532 (1936); Chevallier A. and Dubouloz, P., *Bull. soc. chim. biol.*, **18**, 1115 (1936).

Chevallier uses the changes in absorption at 3250A during irradiation in a method for the spectrographic assay for vitamin A.[96]

Dried spinach loses 70 per cent of its vitamin A during fifteen months of storage in diffused light. Ultraviolet light also decolorizes a petroleum ether extract of carrots and destroys its vitamin A action.[97] Alfalfa leaves bleached in sunlight also show a loss of vitamin A.[98] The same is true of ghee.[99]

The decolorization of carotene is also accelerated by ultraviolet light[100] and it may be this which is changed in alfalfa.[101] Some observations on the photoöxidation of α-carotene in ultraviolet light, reported by Baur,[102] indicate an induction period, after which the course of the oxygen uptake in chloroform solution is autocatalytic. There may be a reversible formation of a photo-oxide. The changes in absorption spectra of carotene and xanthophyll have been followed during their slow oxidation by McNicholas.[103]

Kuhn and Winterstein[104] have isolated from saffron a dimethyl ester of a substance isomeric with crocetin. It is converted into crocetin by the action of blue or violet, but not of red, light. Radiations of wave-lengths less than 4150A are not essential to the reaction. The isomerization may be of the *cis-trans* type.

Vitamin E.[105] Ultraviolet irradiation destroys absorption bands at 2860 to 3200A at the same time that the activity of a concentrate is diminished, according to Bowden and Moore.[106] Bands at 2400 to 2850A are unaltered. The association of a band at 2940A with the biological activity is confirmed by Drummond, Singer and MacWalter,[107] who also find it to be diminished by irradiation. Olcott,[108] however, believes this band due not to the vitamin but to some closely related, difficultly removable substance.

Extracts of the antihemorrhagic vitamin retain their potency after 24 hours of exposure in a sealed tube to the light of a 500-watt lamp at three to four inches.[109] Later, Almquist[109a] showed direct sunlight to destroy the vitamin.

The protective factor against nutritional encephalomalacia in chicks is also resistant to ultraviolet irradiation.[110]

PHOTOCHEMISTRY OF VISION.

It is only possible to note briefly that there has recently been a growing interest in the mechanism of vision. The photochemical changes involved are believed to occur in substances in two different histological structures, the rods scattered throughout much of the retina but particularly toward the periphery, and the cones localized near the fovea.[111] The changes in the former, effected principally during vision in dim light, are not concerned with color sensation, as are the changes in cones which are brought about primarily by bright light.

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[96] Chevallier, A., *Z. Vitaminforsch.*, **7,** 10 (1938); *Chem. Abs.*, **32,** 5016 (1938).

[97] Quinn, E. J., Hartley, J. G., and Derow, M. A., *J. Biol. Chem.*, **89,** 657 (1930).

[98] Smith, M. C., and Briggs, I. A., *J. Agr. Research*, **46,** 229, 235 (1933), *Chem. Abs.*, **27,** 235 (1933); Douglass, E., Tobiska, J. W., and Vail, C. E., *Colorado Agr. Exp. Sta., Tech. Bull.* **4,** 68pp. (1933); *Chem. Abs.*, **28,** 3449 (1934).

[99] Banerjee, B. N., and Dastur, N. N., *Agr. Live-Stock, India*, **6,** 433 (1936); *Chem. Abs.*, **31,** 471 (1937).

[100] Olcovich, H. S., and Mattill, H. A., *J. Biol. Chem.*, **91,** 105 (1931); *Chem. Abs.*, **25,** 3697 (1931).

[101] Russell, W. C., Taylor, M. W., and Chichester, D. F., *New Jersey Agr. Exp. Sta. Bull. 560*, 1 (1934); *Chem. Abs.*, **28,** 6788 (1934).

[102] Baur, E., *Helv. Chim. Acta*, **19,** 1210 (1936); **20,** 402 (1937).

[103] McNicholas, H. J., *Bur. Standards J. Research*, **7,** 171 (1931).

[104] Kuhn, R., and Winterstein, A., *Ber.* **66B,** 209 (1933).

[105] For tentative absorption spectra, Bowden, F. P., and Moore, T., *Nature*, **121,** 512 (1933); von Euler, H., Hellström, H., and Klussmann, E., *Svensk Kem. Tid.*, **45,** 132 (1933); *Chem. Abs.*, **27,** 4284 (1933); Morton, R. A., and Edisbury, J. R., *Nature*, **131,** 618 (1933); Martin, A., Moore, T., Schmidt, M., and Bowden, F. P., *Ibid.*, **134,** 214 (1934).

[106] Bowden, F. P., and Moore, T., *Nature*, **132,** 201 (1933).

[107] Drummond, J. C., Singer, E., and MacWalter, R. J., *Biochem. J.*, **29,** 456 (1935).

[108] Olcott, H. S., *J. Biol. Chem.*, **110,** 695 (1935).

[109] Almquist, H. J., *J. Biol. Chem.*, **114,** 241 (1936).

[109a] Almquist, H. J., *J. Biol. Chem.*, **117,** 517 (1937); MacCorquodale, D. W., Binkley, S. B., McKee, R. W., Thayer, S. A., and Doisy, E. A., *Proc. Soc. Exptl. Biol. Med.*, **40,** 482 (1939).

[110] Goettsch, M., and Pappenheimer, A. M., *J. Biol. Chem.*, **114,** 673 (1936).

The processes are regarded as deviations from photochemical stationary states set up during the period of accommodation to light of various intensities. Little is known as yet as to the photochemistry of materials in the cones.[112] The possibility that a flavin, known to occur in the retina, may be concerned with color vision and thus have to do in some manner with processes occurring in the cones has been mentioned by Theorell.[113]

Since the pioneering observations of Boll in 1877 [114] it has been known that the rods contain a substance known as the visual purple, which is bleached by light. Weigert and Nakashima [115] investigated the photodichroism of the product as obtained from the retinas of frogs and spread in gelatin layers upon glass plates.

When applied to photographic plates, the visual purple usually diminishes rather than increases their sensitivity, but Kögel,[116] who reviewed the photochemical behavior of this material, observed a transient sensitization in a special case.

The bleaching of visual purple solutions in monochromatic light has been found to have a quantum efficiency of unity or very slightly less.[117]

The process is not one of oxidation, according to Brunner and Kleinau.[118] The oxidation-reduction potential curves of solutions of visual purple have been investigated by Pincussen, Suzuki and Seitz.[119] Kodama [120] has measured the glucolysis and oxygen consumption of the rat retina in light and in darkness. During the first thirty minutes, both the oxygen uptake and the aerobic glucolysis were much greater in darkness, but during the second thirty minutes the oxygen uptake diminished rapidly and approached the rate in light. The oxygen consumption was not proportional to the intensity of light with either continuous or short exposures. Aerobic glucolysis was but little influenced by the intensity of light. The gas exchange and oxygen consumption decreased temporarily in all cases in light, the latter showing the greater decrease. In colored light, the oxygen consumption was greatest in red, less in green and least in blue light. Aerobic glucolysis varied less, but in the same order. In sugar-free Ringer solution in darkness, the oxygen consumption was high at first but rapidly decreased to zero. The aerobic glucolysis was very low and quickly dropped to zero. In the presence of 0.1 per cent sugar in the Ringer solution in darkness, the oxygen consumption, high at first, rapidly decreased to one-fifth of its original value, but the aerobic glucolysis decreased but slightly. In the presence of 0.4 per cent of sugar, the oxygen uptake and aerobic glucolysis were comparatively low at the start and decreased but very little. In darkness, anaerobic glucolysis was equally high in solutions containing 0.1, 0.2 and 0.4 per cent of sugar. Jongbloed and Noyons,[121] also found the carbon dioxide production by frog retinas 22.5 per cent and the oxygen uptake 26.5 per cent greater in darkness than in white light.

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[111] Hecht, S., *Physiol, Rev.*, **17**, 239 (1937); *J Applied Phys*, **9**, 156 (1938); Hartline, H. K., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 245 (1935).

[112] von Studnitz, G., *Arch. ges. Physiol (Pflüger's)*, **239**, 515 (1937). Wald, G. [*Nature*, **140**, 545 (1937)] calls the violet cone pigment iodopsin. Vitamin A is probably related to it. Haig, C., Hecht, S and Patek, A. J., Jr., *Science*, **87**, 534 (1938); Hecht, S. and Mandelbaum, J., *Ibid.*, **88**, 219 (1938).

[113] Theorell, H., *Biochem. Z.*, **279**, 186 (1935).

[114] Boll, F., *Arch. anat. Physiol*, 4 (1877).

[115] Weigert, F., and Nakashima, M., *Naturwiss*, **17**, 840 (1929).

[116] Kögel, G., *Phot. Korr.*, **65**, 138, 248 (1929); *Chem. Abs.*, **24**, 2068 (1930). Recent studies on the absorption spectrum of visual purple are due to Chase, A. M., and Haig, C., *J. Gen. Physiol.*, **21**, 411 (1938) and to Saito, Z., *Tohôku J. Exptl. Med.*, **32**, 432 (1938); *Chem. Abs.*, **32**, 9125 (1938).

[117] Dartnall, H. J. A., Goodeve, C. F., and Lythgoe, R. J., *Proc. Roy. Soc.*, **A156**, 158 (1936); **A164**, 216 (1938); Lythgoe, R. J., and Goodeve, C. F., *Trans. Ophthalmol. Soc.*, **57**, 88 (1937); Goodeve, C. F., *Sci. J. Roy. Coll. Sci.*, **8**, 9 (1938).

[118] Brunner, O., and Kleinau, W., *Monatsh.*, **68**, 244, 261 (1936).

[119] Pincussen, L., Suzuki, T., and Seitz, E. O., *Biochem. Z.*, **272**, 357 (1934).

[120] Kodama, S., *Tohôku J. Exptl. Med.*, **28**, 423 (1936); *Chem. Abs.*, **31**, 1081 (1937).

Stutzke[122] observed that when the dark-adapted beef retina is exposed to light, ammonia is liberated, the ammonia content increasing from 200 to 500 per cent. This effect, which can be inhibited by glucose, lactate or pyruvate, is not observed in the light-adapted retina.

More recent studies of the behavior of the visual purple have revealed intimate relationships not only to such compounds as trimethylamine and creatinine, but also to carotenes, vitamin A, and the flavins.[123]

Observations on night blindness, a vitamin A deficiency,[124] led to the discovery of vitamin A in the normal retina. Wald[125] showed that mammalian retinas contain about 22 γ, and frog retinas 400 γ per gram of dry retina. The underlying pigment layers contain also xanthophyll. The function of the vitamin A is to serve as a precursor for the formation of the visual purple which is lost in the photochemical bleaching process. There is also present in the retina a faintly yellow pigment, known as retinene, of carotenoid nature. It does not occur free but associated with some other non-diffusible substance, probably a protein. In the light-adapted retina, the retinene is replaced by some vitamin A.

During vision the visual purple is converted photochemically into visual yellow which contains protein and retinene. This change is believed to be thermally reversible with regeneration of visual purple. Mirsky[126] suggests that the prosthetic group, retinene, is firmly bound in visual purple, and that the process of its bleaching to visual yellow consists in a denaturation of the protein after which the retinene is bound loosely if at all He concludes the energy of activation of the denaturation to be low, the visual purple being denatured by a quantum of visible light. The function of the retinene in the visual purple may be to sensitize the protein denaturation to light.

When the visual yellow has been produced, it may either regenerate its precursor or lose some of its retinene which is then thermally converted into vitamin A and apparently lost to the retina by diffusion processes or in an unknown manner This loss of visual purple has to be made up if night-blindness is to be averted, by a resynthesis by way of the underlying pigmented layer which Wald has shown to contain larger amounts of vitamin A. At least this is the case in the frog's eye, the retina of which has no blood supply.[127]

Details of the effects of temperature, pH and seasonal variations on the bleaching of visual purple have been reported by Chase,[128] who finds a photochemical decomposition product of certain retinal extracts to be an acid-base indicator, yellow in acid and colorless in alkaline solutions. He also states that the photodecomposition of the bile salt extracts of the retinas of summer frogs follows a first-order reaction course, but that of the extracts of winter frogs does not unless the extracts are made alkaline. The kinetics of the regeneration of bleached visual purple have recently been studied by Hecht, Chase, Schlaer and Haig.[129]

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[121] Jongbloed, J., and Noyons, A, *Z. Biol.* **97**, 399 (1936); *Chem. Abs.*, **31**, 2691 (1937).

[122] Stutzke, S., *Klin. Wochschr.*, **15**, 524 (1936); *Chem. Abs.*, **30**, 6805 (1936).

[123] Brunner, O., *Oesterr Chem. Ztg.*, **40**, 203 (1937); Wald, G., and Zussman, H, *Nature*, **140**, 197 (1937).

[124] Blegvad, O., *Am. J. Ophthalmol*, **7**, 89 (1924); Fridericia, L. S., and Holm, E., *Am. J. Physiol.*, **73**, 63 (1925).

[125] Wald, G., *J. Gen. Physiol.*, **18**, 905 (1935); **19**, 781 (1936); *Nature*, **134**, 65 (1934).

[126] Mirsky, A. E., *Proc. Natl. Acad. Sci*, **22**, 147 (1936). Krause, A. C., and Sidwell, A. E., Jr. *Am. J. Physiol.*, **121**, 215 (1938); *Arch. Ophthalmol.*, **18**, 807 (1937); suggest that the bleaching splits visual purple into protein and a colored lipid called visual yellow, which may be further bleached until colorless.

[127] See also Wald, G., and Clark, A.-B., *J. Gen. Physiol.*, **21**, 93 (1937).

Some attention has been devoted to the nature and function of other pigments, such as the orange intermediate between visual purple and the products of its complete bleaching,[130] and also to a blue-sensitive substance, possibly a flavin, which Chase believes may, after its decomposition, be concerned in the regeneration of the visual purple.[131]

Porphyropsin, a purple pigment from the retina of fresh-water fish, also goes through a cycle in light, involving russet and yellow pigments.[132] Stern and Salomon,[133] suggest that the first step in the bleaching of visual purple may be a photodissociation of ovoverdin, rather than a denaturation of the protein carrier.

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[128] Chase, A. M., *J. Gen. Physiol.*, **19**, 577 (1936). See also Lythgoe, R. J., *J. Physiol.*, **89**, 331 (1937), Wald, G., *J. Gen. Physiol.*, **21**, 795 (1938).

[129] Hecht, S., Chase, A. M., Schlaer, S., and Haig, C., *Science*, **84**, 331 (1936). See also Hecht, S., Chase, A. M., and Shlaer, S., *Ibid.*, **85**, 567 (1937).

[130] Wald, G., *Nature*, **139**, 587 (1937).

[131] Chase, A. M., *Science*, **85**, 484 (1937).

[132] Wald, G., *Nature*, **139**, 1017 (1937).

[133] Stern, K. G., and Salomon, K., *Science*, **86**, 310 (1937)

Chapter 42

Photosensitized Biological Processes

The existence of a number of photosensitized reactions (discussed in Chapter 16) leads to the expectation that similar effects are to be encountered in biological processes. The first instance was reported by Raab from the laboratory of v. Tappeiner in 1899.[1] He observed that the dye acridine, in a dilution of 1:20,000, killed paramecia in six minutes in direct sunlight, in an hour in diffused light, and remained without effect for long periods in darkness. Many other dyes of widely different classes have similar effects, to which v. Tappeiner[2] applied the term "photodynamic actions."

Many recent workers have studied similar lethal effects on bacteria,[3] fungi[4] and various bacteriophages and viruses,[5] as well as the destructive effects upon their toxins.[6]

The hemolysis of red cells may be similarly sensitized,[7] notably by chlorophyll, which is effective even in dilutions of one in thirty million.[8] Hematoporphyrin, a product of the decomposition of hemoglobin, as well as other porphyrins, exhibits such properties in a marked degree.[9] When it is injected into mice no effects are produced until the animals are irradiated by sunlight or a carbon arc. Light causes itching, hyperemia of the ears, tail and snout, and, with sufficient doses of the sensitizer, the animals may die in light-stroke in a tetanic rigor. Desensitization occurs in darkness in about two weeks. The subject has been investigated to a considerable extent.[10]

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[1] v. Tappeiner, H., *Z. Biol*, **39,** 524 (1900)

[2] v. Tappeiner, H, *Deut. Arch. klin. Med.,* **80,** 427 (1904).

[3] Brocq-Rousseau, D, *Compt rend soc. biol.,* **119,** 272 (1935), *Chem. Abs*, **29,** 5474 (1935); Szüts, A., *Magyar Orvosi Arch.,* **33,** 267 (1932), *Chem. Abs*, **27,** 323 (1933); Vorster, D., *J Dental Research,* **9,** 641 (1929); *Chem. Abs*, **24,** 133 (1930); Philibert, A. and Risler, J., *Compt. rend.,* **183,** 1137 (1926), **186,** 1152 (1928); Ram, A, *Proc. Acad Sci. United Provinces, Agra, Oudh, India,* **4,** 83 (1934); Bovet, D., *Helv Chim. Acta,* **17,** 1460 (1934); T'ung,, T., and Zia, S. H. *Proc. Soc. Expt. Biol Med*, **36,** 326 (1937), Beck, L V., and Nichols, A. C., *J. Cellular Comp. Physiol*, **10,** 123 (1937); T'ung, T., *Proc. Soc. Exptl Biol. Med.,* **38,** 29 (1938); Chin, T. L, *Ibid.,* **38,** 697 (1938).

[4] Gomez-Vega, P., *Arch. Dermatol Syphilol.,* **32,** 49 (1935); *Chem. Abs.,* **30,** 572 (1936).

[5] Clifton, C. E., *Proc. Soc. Exptl. Biol Med.,* **28,** 745 (1931); Linden, H., and Schwarz, F. K. T., *Arch. Hyg.,* **106,** 133 (1931); Prescher, W., *Planta (Abt. E., Z. wiss. Biol.),* **17,** 461 (1932); *Chem. Abs*, **27,** 3968 (1933); Perdrau, J. R, and Todd, C., *Proc. Roy. Soc.,* **112B,** 188, 277 (1933); Galloway, T. A., *Brit. J Exp. Path.,* **15,** 97 (1934); Storey, H. H. *Ann. Applied Biol.,* **21,** 588 (1934); *Chem. Abs.,* **29,** 2203 (1935); Sheboldaeva, A D., and Shugladze, A. K., *Z Microbiol. Epidemiol. Immunitatsforsch. (U.S.S.R.),* **18,** 466 (1937); *Chem. Abs.,* **32,** 7504 (1938).

[6] Lippert, K. M., *J Immunol*, **28,** 193 (1935); *Chem. Abs*, **29,** 8048 (1935).

[7] Gachs, H., and Sacharoff, G, *Munch. Med. Wochschr.,* **52,** 297 (1905); Saeki, K., *Japan J. Gastroenterol.,* **4,** 153, 166, 231, 244 (1932); *Chem. Abs.,* **27,** 1018 (1933); Angelica, V., *Boll soc. ital. biol. sper.,* **8,** 1536 (1933); *Chem. Abs.,* **28,** 2767 (1934); Blum, H. F., Pace, N., and Garrett, R. L., *J. Cellular Comp. Physiol*, **9,** 217 (1937).

[8] Hausmann, W., *Jahr. Wiss Botanik,* **46,** 599 (1909).

[9] Kammerer, H., and Weisbecker, H., *Arch. Exptl. Path. Pharmakol.,* **111,** 263 (1926); Squires, B. T., *Biochem. J.,* **21,** 437 (1927).

[10] Hausmann, W., and Löhner, L., *Biochem. Z.,* **173,** 7 (1926); Fabre, R., and Simonnet, H., *J. pharm. chim.,* **4,** 294 (1926); Supniewski, J. V., *J. Physiol.,* **64,** 30 (1927); *Chem. Abs.,* **22,** 455 (1928); Rock, E N., and Howell, W. H., *Am. J. Physiol.,* **84,** 363 (1928); Smetana, H., *J. Exptl. Med.,* **47,** 593 (1928); Cuzin, J., *Bull. soc. chim. Biol.,* **12,** 1401 (1930); *Chem. Abs.,* **25,** 3368 (1931); Quin, J. I., *Rept. Director Vet. Services Onderstepoort,* **17,** Pt. 2, 645 (1931); *Chem. Abs.,* **27,** 5421 (1933); Szörenyi, E. T., *Biochem. Z.,* **252,** 113 (1932); *Boll. soc. ital. biol. sper.,* **7,** 835, 866 (1932); Robuschi, L., *Biochem. terap. sper*, **23,** 54 (1936); *Chem. Abs.,* **30,** 5245 (1936); Hausmann,

Meyer-Betz[11] took 0.2 gram of hematoporphyrin intravenously. Irradiation by a carbon arc led to the production of a lesion which had some resemblance to those of hydroa. The immediate reaction was merely reddening and edema, but on the following day the area was infiltrated, reddened and painful, and rendered almost black by multiple hemorrhages. After a week, there was superficial necrosis, followed by the formation of a thick black scab. The sun produced on exposed areas a very severe dermatitis which began immediately after the exposure and progressed for several days. It was marked by extreme pain, swelling and induration, and was followed by a heavy pigmentation. Two cases of chronic porphyrinuria have recently been reported in which the face and hands were highly pigmented, although not hypersensitive to ultraviolet light.[12]

A disease in which there is marked sensitivity to light is the rare and usually fatal xeroderma pigmentosum or Kaposi's disease.

In human pathology, true light urticarias are rare.[13] It has been suggested that hydroa vacciniforme represents a slight sensitization due to hematoporphyrin or other porphyrins produced by solar ultraviolet light from some precursor which was assumed to be present in the skin. The basis for this theory of the origin of the disease is the frequent association of a porphyrinuria. It may, however, be noted that porphyrinuria may occur from certain causes without causing light sensitivity.[14]

Certain diseases of animals have been attributed to photosensitization. After eating buckwheat, and especially the green parts of the plant, oxen, swine and sheep, on exposure to light, become greatly excited and dance about wildly because of the sensory stimulation of rapidly developing skin lesions. This disease, known to Hertwig as early as 1833, has been studied by Sheard, Caylor and Schlotthauer,[15] who suggest that the sensitizer may be phylloporphyrin or possibly cholehematin.

The weed, St. John's wort, Hypericum, brings about similar symptoms in range animals, and it has been stated that Arabs used to stain their white horses with tobacco or henna to protect them from light in regions where this weed abounds. Ionnides[16] isolated a pigment from the plant which photosensitized white rats, but its constitution is unknown.

A disease of sheep and Angora goats, Geelgikop, characterized by the sudden onset of a swelling of exposed parts of the head and ears,[17] is caused by eating *Tribulus terrestris*.

W., and Kuen, F. M., *Biochem Z.*, **265**, 105 (1933); Guerrini, G, *Boll soc. ital. biol sper.*, **6**, 401 (1931); *Chem. Abs.*, **26**, 772 (1932). Other substances may act, as trypaflavine, John, H, [*Biochem, Z.* **155**, 159 (1925)], bacterial extracts, Risler, J., and Philibert, A, [*Compt. rend soc biol*, **96**, 747 (1927); *Chem. Abs.*, **21**, 1844 (1927)], and bile, Condorelli, F., *Arch. fisiol.*, **28**, (1930); *Chem. Abs*, **25**, 3711 (1931)

[11] Meyer-Betz, F., *Deut. Arch. Klin. Med.*, **122**, 476 (1913).

[12] Roth, E., *Deut. Arch. Klin. Med.*, **178**, 185 (1935). For congenital porphyrinuria in cattle, Rimington, C., *Onderstepoort J. Vet Sci. Animal Ind.*, **7**, 567 (1936); *Nature*, **140**, 105 (1937); *Chem. Abs.*, **31**, 7108 (1937); Fröhlich, W., *Wien. Klin. Wochschr.*, **51**, 791 (1938); *Chem. Abs.*, **32** 8510 (1938)

[13] The relation of sensitization to light to dermatology has been reviewed by Eidinow, A., *Proc. Roy. Soc. Med.*, **28**, 633 (1935); Mathews, F. P, *Arch. Path.*, **23**, 399 (1937); *Chem. Abs*, **31**, 5430 (1937). See also Ambroglio, A., *Arch ital. dermatol. sifilog. venereol.*, **13**, 546 (1937); *Chem. Abs.*, **32**, 2216 (1938); Urbach, F., *Klin. Wochschr.*, **17**, 304 (1938); *Chem Abs.*, **32**, 7116 (1938)

[14] Hausmann, W., and Kuen, F. M., *Biochem. terap. sper.*, **21**, 441 (1934), *Chem. Abs.*, **29**, 1875 (1935).

[15] Sheard, C., Caylor, H. P., and Schlotthauer, C. P., *J. Exptl. Med.*, **47**, 1013 (1928).

[16] Ionnides, Z. M, *Arch. Inst Pasteur Hellen.*, **2**, 161 (1928); *Chem. Abs.*, **25**, 1869 (1931), *Compt. rend soc. biol.*, **105**, 349 (1930); *Chem. Abs*, **25**, 1869 (1931)

[17] Quin, J. I., and Rimington, C., *South African J. Sci.*, **30**, 461 (1933), *Chem Abs*, **28**, 2056 (1934); Quin, J. *Onderstepoort J. Vet. Sci.*, **1**, 459, 469, 497, 501, 505 (1933); **3**, 137 (1934); **4**, 463; *Chem. Abs.*, **28**, 2790 (1934); **29**, 7351 (1935); Rimington, C, Quin, J. I., and Roets, G. C. S., *Onderstepoort J. Vet. Sci. Animal Ind.*, **9**, 225 (1937); *Chem. Abs.*, **32**, 4660 (1938).

A wide variety of other physiological and pathological effects due to the action of light and sensitizers has been enumerated by Blum.[18] Among others mentioned are the inhibition of clotting of the blood by fibrinogen in the presence of light and methylene blue, stimulation of nerves, contraction of isolated skeletal muscles bathed by the photosensitizer solution, and production of arythmias in the isolated turtle or mammalian heart perfused with photosensitizing solutions and exposed to light.

The hydrolysis of serum albumin may be effected by hematoporphyrin and oxygen in light.[19] The porphyrin unites with the protein, becomes excited by the absorption of light, combines with oxygen and passes a part of its energy over to the protein molecule.

A number of generalizations have been made by Blum regarding these processes.[20] Although most sensitizers are fluorescent, the fluorescent rays they emit are not responsible for the effects produced and there is no quantitative relation between the fluorescence of a sensitizer and its biological effectiveness. The substances absorb chiefly in the visible range, and only the absorbed energy is effective biologically. (The possibility of sensitization to ultraviolet rays cannot be excluded.) Most of the effects produced by these substances in light can also be produced by them, although much more slowly, in darkness. The presence of oxygen appears to be essential for the processes occurring in light.[21] Most effects in this category can be inhibited by blood serum and particularly by its albumin. Because of this action, the injection of dyes which hemolyze red blood cells *in vitro* is not followed by hemolysis in animals subsequently exposed to light.

Sensitization to various ultraviolet radiations may be effected by certain substances, such as acridine or trypaflavine, which make the region in the vicinity of 3650A active.[22] Ethyl chlorophyllide sensitizes especially to 3130 or 3650A, as well as to visible rays. Carotene sensitizes to the range of 2800 to 4350A, but in the shorter ultraviolet or visible rays is less effective than chlorophyll.[23]

Attempts to utilize photodynamic substances in therapy have not proved encouraging. Kreidl and Nozicka [24] suggest that the therapeutic action of light may be promoted by injecting anthracene, anthraquinone or their derivatives. Eosin was at one time believed to cause a rapid loosening of necrotic tissues in luetic or tuberculous ulcers on exposure to sunlight. In connection with such attempts, it may be noted that urticarial reactions are readily produced. The intradermal injection of two drops of a 1:1000 solution of eosin renders the skin so sensitive that a few minutes of exposure to light produces an urticarial wheal.

An understanding of the mechanism of photosensitized biological processes is of importance because of the light it may cast upon the nature of the function of chlorophyll in the photosynthesis of carbohydrates. Noack [25] early divided photosensitizers into two classes: certain heavy metal salts and fluorescent organic dyes. Both serve as carriers of oxygen, the former by a change in valence of the metal and the latter by a formation of peroxides. The action of the latter substances can be stopped by such reducing agents as sodium sulfite. Gaffron[26] found that solutions of hematoporphyrin, chlorophyll or dyes in serums at pH 11.4 absorb oxygen on exposure to light with the oxidation of the protein to which the dyes become attached. Carbon dioxide and ammonia are liberated. The greater part of the former is ascribed to the action of acids liberated during oxidation upon the serum. Tyrosine, phenol and uric acid in alkaline solution can also be oxidized in this manner by dyes, such as eosin, erythrosin or Rose bengal. Aliphatic substrates are not so oxidized, according to Carter.[27] The introduction of an hydroxy or an amino-group renders benzene derivatives susceptible to this type of reaction. Side-chains in which the groups NH_2 and $CH{=}CH$ occur were oxidized, as were ring compounds, such as α-naphthol, tryptophane, tyrosine, thiophene and purine derivatives. Carter did not believe that hydrogen peroxide is formed in the process, which was neither accelerated by iron salts nor retarded by potassium cyanide.[28] Some have found such processes to be increased by cyanide.[29] Wohlgemuth and Szörényi believe that true tissue respiration is lowered from 2 to 18 per cent by visible or ultraviolet light. Sensitizers in darkness also reduce it. Illumination of tissue sections in the presence of hematoporphyrin or Rose bengal increases oxidation and this action is stimulated by cyanides. The true respiration, which they regard as distinct from this photoöxidation, is believed to be reduced from 17 to 43 per cent. Sensitizers also decrease the usual stimulating effect of light on anaerobic glycolysis. In red cells, sensitizers produce methemoglobin especially when illuminated.[30] Hematoporphyrin increases the absorption of oxygen by red blood cells, especially in light, but there is no corresponding production of carbon dioxide. Photographic desensitizers as Pinakryptol green retard this.[31] Attempts to isolate peroxides of fluorescent dyes which promote the transportation of oxygen in analogy with the assumed chlorophyll peroxide of Willstätter were unsuccessful, according to Gaffron.[32] Acceptor peroxides were, however, produced during the photoöxidation of aliphatic amines in the presence of chlorophyll. When a solution of chlorophyll in amylamine was exposed to light and then placed in darkness, the quantity of peroxidic oxygen was approximately equal to the amount of molecular oxygen absorbed. This oxygen was quantitatively evolved when a catalyst, such as manganese dioxide was added to the darkened solution. The photochemical action depended greatly upon the solvent chosen, increasing more than a hundred times when acetone or pyridine replaced water. The absorption of oxygen ultimately reached two molecules for each molecule of primary or secondary amine. Gaffron[33] dissolved ethyl chlorophyllid and allylthiourea in acetone and exposed the solution to monochromatic light in the presence of oxygen. The relation between the energy absorbed and the oxygen consumed was in agreement with the Einstein law, provided that the concentration of the acceptor was at least 7.5×10^{-1} moles per liter, or when the acceptor concentration was over 100 times that of the dye. Similar results were reported with hematoporphyrin as the dye.

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[18] Blum, H. F., *Physiol. Rev.*, **12**, 23 (1932); Sellards, S. W., *J. Med. Research*, **38**, 293 (1918); Dognon, A., *Compt. rend. soc. biol.*, **98**, 283 (1928).

[19] Boyd, M. J., *J. Biol. Chem*, **103**, 249 (1933).

[20] See also Blum, H. F., *Biol. Bull.*, **59**, 81 (1930); *Chem. Abs*, **26**, 4645 (1932).

[21] Blum, H. F., and McBride, G. C., *Biol. Bull*, **61**, 316 (1931); *Chem. Abs.*, **26**, 2523 (1932); Blum, H. F., *J. Cellular Comp. Physiol.*, **9**, 229 (1937); Spealman, C. R, and Blum, H. F., *Univ. Calif Pub. Physiol.*, **8**, 147 (1937).

[22] Kuen, F. M., and Rosenfeld, P., *Biochem Z*, **254**, 181 (1932)

[23] Kuen, F. M., and Püringer, K., *Biochem Z.*, **286**, 196 (1936).

[24] Kreidl, I., and Nozicka, F, Austrian Patent, 142,163, June 25, 1935; *Chem. Abs.*, **29**, 6365 (1935). The claims that hematoporphyrin can enable visible light to cure rickets are doubtless in error in view of the work of Windaus on sensitized reactions of ergosterol. (Chapter 39.) Rezzesi, F. D., *Biochem. terap. sper.*, **24**, 274 (1937); *Chem. Abs.*, **32**, 650 (1938). Tests by Marique, P. [*Bull soc. chim. biol.*, **20**, 325 (1938); *Chem. Abs.*, **32**, 5039 (1938)] gave negative results.

[25] Noack, K., *Z. Botan.*, **12**, 273 (1920); *Chem. Abs.*, **15**, 2453 (1921).

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[26] Gaffron, H., *Naturwiss.*, **13**, 859 (1925); *Biochem. Z.*, **179**, 157 (1926).

[27] Carter, C. W., *Biochem J.*, **22**, 575 (1928).

[28] See also Blum, H. F., and McBride, G. C., *Biol. Bull.*, **61**, 316 (1931); *Chem. Abs.*, **26**, 2523 (1932).

[29] Bier, O. G., and Roche e Silva, M., *Compt. rend. soc. biol.*, **118**, 911, 914 (1935); *Chem Abs.*, **29**, 3727 (1935); Wohlgemuth, J., and Szörényi, E., *Biochem. Z.*, **264**, 371, 389, 406 (1933).

[30] See also Chocetta, A., *Boll. soc. ital. biol. sper.*, **7**, 1545 (1932); *Chem. Abs.*, **27**, 2731 (1933).

[31] Szörényi, E., *Biochem. Z.*, **252**, 113 (1932). See also Smetana, H., [*J. Biol. Chem.*, **124**, 667, 741, 745 (1938)] who finds the proteins of blood and the uric acid of urine the acceptors.

[32] Gaffron, H., *Ber.*, **60B**, 2229 (1927).

[33] Gaffron, H., *Ber.*, **60B**, 755 (1927).

Blum and Spealman[34] believed the peroxide formed when fluorescent dyes alone are irradiated in aqueous solutions to be hydrogen peroxide formed from water and oxygen. They suggest that the bleaching of excited dye molecules may be due to their oxidation by the hydrogen peroxide.

There has been much discussion as to whether, in the dye-sensitized oxidations of various substances, it is the oxygen itself or the oxygen acceptor which receives the energy of the light-excited dye. Gaffron[35] does not believe the former can account for the facts. Even in cases in which it is the sensitizer itself which is oxidized, Gaffron believes that there are other molecules of the sensitizer which receive enough energy from the light-excited molecules to convert them into a long-lived form capable of being oxidized. Data on the quantum yields in the oxidation of rubrene were advanced in support of this view, but have recently been the subject of some discussion. (See Chapter 26.)

On the other hand, Kautsky and Hirsch,[36] in work on the oxidation of isoamylamine in the presence of chlorophyll, assumed that oxygen was activated by the transfer of energy from a metastable intermediary state of the pigment. The energy required for the activation of oxygen was calculated to be 37 kcal. (7620A). Energy of longer wave-lengths should not be able, therefore, to cause the reaction. To test this, Gaffron[37] filtered out practically all light of wave-length shorter than 7600A by the use of 6 mm. of B G 3, Schott glass. Bacterial pheophytin was used, since chlorophyll does not absorb in this range; thiosinamine was the acceptor. Since photoöxidation still occurred, it seems that activation of oxygen is not the mechanism, and it must be the acceptor molecules which receive the energy of the excited dye. When organic substrates are oxidized in the presence of chlorophyll, one molecule of oxygen is used for each quantum of light absorbed regardless of the wave-length, except at wave-lengths where the quantum is too small and the reaction does not proceed. Further evidence that it is the oxygen-acceptor which acquires the energy has been given by Franck and Levi.[38] They suggest that the chlorophyll on absorption may form hydrogen and free radicals instead of forming a metastable excited molecule. These may subsequently reunite, with the production of a chemiluminescent glow. In the presence of oxygen, the hydrogen is oxidized. The acceptor takes over the energy absorbed by the chlorophyll. This offered a possible explanation of the fact that the fluorescence, which represents but a small part of the energy, is slightly extinguished by oxygen. The problem is still in a somewhat speculative state. Because of its relation to other photosensitized processes by which carbon dioxide and water are synthesized to carbohydrates in the green plant, the mechanism of these reactions is being actively investigated.

By continuously irradiating a dilute solution of sodium fluorescein, Menke[39] made a photofluorescein. It was separated by filtering after precipitation with a small amount of hydrochloric acid. After washing with water, the precipitated dye was dissolved in alkali and the sodium salt crystallized by careful evaporation. This material was then dissolved in Locke's solution so that each cc. contained a mg. of photofluorescein. It then hemolyzed rat blood in darkness to the same extent that fluorescein does in light, although the non-irradiated fluorescein had no apparent action in darkness. Approximately two hours in darkness were required for a 1:2000 dilution of the photofluorescein to hemolyze one cc. of 1 per cent red blood cells. Blum[40] believes that eosin dyes in dilute solutions show hemolysis of red blood cells in darkness only in the presence of hydrogen peroxide.

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[34] Blum, H. F., and Spealman, C. R., *J. Phys. Chem.*, **37**, 1123 (1933).

[35] Gaffron, H., *Biochem. Z.*, **264**, 251 (1933).

[36] Kautsky, H., and Hirsch, A., *Ber.* **64**, 2677 (1931); Kautsky, H., de Bruijn, H., Neuwirth, R., and Baumeister, W., *Ber.*, **66**, 1598 (1933); Kautsky, H., and Hirsch, A., *Biochem. Z.*, **278**, 374 (1935); Kautsky, H., Hirsch, A., and Flesch, W., *Ber.*, **68**, 152 (1935).

[37] Gaffron, H., *Ber.*, **68B**, 1409 (1935); *Chem. Abs.*, **29**, 8056 (1935) .

[38] Franck, J., and Levi, H., *Naturwiss.*, **23**, 229 (1935).

[39] Menke, J. F., *Biol. Bull.*, **68**, 360 (1935); *Chem. Abs.*, **29**, 5871 (1935).

This résumé is necessarily too brief to give an adequate impression of the great number of investigations in this field which are of importance to the zoölogist or botanist rather than to the photochemist.[41]

That eosin and hematoporphyrin, when applied to the skin of mice and exposed for three months to sunlight, may produce skin tumors, has been noted by Büngeler.[42] Certain carcinogenic agents, such as benzopyrene, shale oil and coal tar, exhibit a photodynamic action on paramecia.[43]

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[40] Blum, H. F., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 318 (1935).

[41] See, for further details: Kosman, A. J., and Lillie, R. S., *J. Cellular Comp. Physiol*, **6**, 505 (1935); *Chem. Abs.*, **29**, 8098 (1935); Hinrichs, M., *Biol. Bull.*, **50**, 1 (1926); Guerrini, G., *Boll. soc. ital. biol. sper.*, **8**, 1357 (1933); *Chem. Abs.*, **28**, 1726 (1934); Macht, D. I., *Proc. Soc. Exptl. Biol. Med.*, **23**, 638, 639 (1926); Sunzeri, G., *Arch. fisiol.*, **33**, 555 (1934); *Chem. Abs.*, **29**, 1883 (1935); Welsh, J. H, *Biol. Bull*, **66**, 346 (1934); *Chem. Abs.*, **28**, 346 (1934); Efimov, A., and Efimov, W. W., *Biochem Z.*, **155**, 376 (1925); Schanz, F., *Ber. botan. Ges.*, **41**, 165 (1923); *Chem. Abs.*, **17**, 3040 (1923); Blum, H. F., and Scott, K. G, *Plant Physiol.*, **8**, 525 (1933); Jirovec, O., and Ziegler, Z., *Z ges. Exptl. Med.*, **90**, 651 (1933); *Chem. Abs*, **29**, 4031 (1935); Zikes, H., *Centr. Bakt. Parasitenk.*, **II**, **65**, 128 (1925); *Chem. Abs.*, **20**, 1423 (1926); Teplov, I. and Dobrokhotova, E., *Arch sci. biol. U.S S.R.*, **32**, 72 (1932); *Chem. Abs.*, **27**, 3492 (1933); Macht, D. I., and Teagarden, E. J., Jr., *J. Pharmacol.*, **22**, 21 (1923); Roskin, G., and Romanova, K., *Z. Immunitäts*, **72**, 445 (1931); *Chem. Abs.*, **26**, 2790 (1932); Azzi, A., *Arch. Sci. Med.*, **45**, 212 (1922); *Chem. Abs.*, **17**, 3541 (1923); Monasterio, G., *Arch. Farmacol. Sper.*, **51**, 111 (1930); *Chem. Abs.*, **25**, 2486 (1931); Spealman, C R., and Blum, H. F., *J Cellular Comp. Physiol.*, **3**, 397 (1933), *Chem. Abs.*, **28**, 3089 (1934); Hinrichs, M. A., and Kosman, A. J., *J. Cellular Comp. Physiol*, **6**, 487 (1935); Lippay, F., *Klin Wochschr.*, **6**, 651 (1927); *Chem. Abs.*, **21**, 2706 (1927); Nitta, B., *Folia Pharmacol. Japon*, **17**, 72 (1928); *Chem. Abs.*, **32**, 3434 (1938); Kosman, A. J, *J. Cellular Comp. Physiol.*, **11**, 279 (1938); *Chem. Abs*, **32**, 6677 (1938); Zia, S. H., Chow, B. F., and T'ung, T., *Proc Soc Exptl. Biol. Med.*, **38**, 688 (1938).

[42] Büngeler, W., *Z. Krebsforsch.*, **46**, 130 (1937); *Chem. Abs*, **31**, 8670 (1937)

[43] Mottram, J. C., and Doniach, I., *Nature*, **140**, 933 (1937); *Lancet*, **I**, 1156 (1938).

Chapter 43

Photosynthesis of Carbohydrates[1]

With the help of sunlight, the green plant builds up from carbon dioxide, water and salts the sugars and starches which serve as the foodstuffs of man. At the same time, oxygen is liberated. The photosynthetic process may be represented by the equation:

$$CO_2 + H_2O + \text{light} \rightarrow CH_2O + O_2.$$

The hypothetical formaldehyde is assumed to be subsequently converted into sugars and starches. The energy required for this endothermic reaction must be supplied as light. This is absorbed by chlorophyll, the green pigment of the leaves, which in some as yet unknown manner acts as a photosensitizer for the reaction. The energy required for the synthesis of formaldehyde is at least 134 kcal., and possibly more.[2] Since the effective wave-lengths in the visible range may be as long as about 7000A, corresponding to only about 40 kcal., it is apparent that the absorption of one quantum per molecule would not provide sufficient energy to supply that needed for the reaction. It is essential, therefore, that at least three and more likely four quanta be absorbed for each molecule of carbon dioxide assimilated or of oxygen liberated. The nature of the coupled series of reactions underlying the photosynthetic process is not as yet understood, although ever-increasing attention has been devoted to the problem.

The investigations in this field may be divided into those concerned with the photochemical mechanism involved, as it might possibly be conceived of as occurring *in vitro* (in the presence of the extracted sensitizing pigment) and into those which actually occur in the plant. The latter studies belong in the realm of the plant physiologist and involve many complicated features, such as the influences of the stomatal openings within the leaf by which the gases gain entrance and egress, the nature and orientation of the chloroplasts (the histological regions within which the chlorophyll occurs), the amounts of energy reflected, absorbed and transmitted by the leaf, etc. For a discussion of these factors special works must be consulted.[3] It is possible here to mention merely some calculations of the efficiency of the process as it occurs in an acre of corn, which have been made by Transeau.[4] Assuming a yield of 100 bushels per acre, 10,000 corn plants on an acre yield a dry weight of 2160 kg. of corn. The total dry weights of the plants at maturity would be about 6000 kg. After deducting 322 kg. of mineral matter there would be a residue of 5678 kg. of organic matter, of which about 2675 kg. is carbon. The glucose equivalent of this is 6678 kg. This is less than the true amount formed, since some would have been consumed in respiration during the life of the plants. This is estimated at 2045 kg. so that the total glucose made by the plants would have been 8732 kg. This is estimated to have required not far from 33 million calories of energy. The total energy of sunlight falling during this period on the acre is estimated as 2043 million calories, so that about 1.6 per cent of the light energy might have been used in photosynthesis. If it be assumed that only about 20 per cent of the incident radiant energy is in the wave-length regions capable of causing photosynthesis, then the overall efficiency of this light would be raised to about 8 per cent. There are several reasons for this low value. There are large reflection losses and some energy is lost by transmission.[5] During a large part of the growing period, much of the energy reaches merely the ground instead of the leaves of the plants, causing a loss estimated for the period at about 54 per cent. Respiration liberates about a quarter of the energy absorbed in the photosynthetic process. Another loss is in the energy required for transpiration. For every kilogram gained in dry weight, about 276 are evaporated during the growing season.

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[1] A recent review is given by W. M. Manning, *J. Phys. Chem.*, **42**, 815 (1938).

[2] Blum, H. F., *Am. Naturalist*, **71**, 350 (1937).

[3] Stiles, W., "Photosynthesis, The Assimilation of Carbon by Green Plants," London, Longmans, Green, 1925; Spoehr, H. A., "Photosynthesis," New York, The Chemical Catalog Co., Inc. (Reinhold Publishing Corp.), 1926; Stiles, W., *Sci. Progress*, **25**, 590 (1931); Baly, E. C. C., *Sci. J. Roy. Col. Sci.*, **2**, 58 (1932).

[4] Transeau, E. N., *Ohio J. Sci.*, **26**, 1 (1926).

Formaldehyde as Intermediate. Von Baeyer[6] seems to have been the first to suggest the formation of formaldehyde in an initial stage of the process. Sabalichschka[7] showed that certain plants, when deprived of carbon dioxide and supplied with formaldehyde, polymerize the latter to sugars and starch, even in the absence of light. From a study of the assimilatory quotient CO_2/O_2, Willstätter and Stoll[8] contend that formaldehyde is the only intermediate possible between carbon dioxide and the carbohydrates. This quotient under all conditions was found experimentally to be one, that indicated by the equation in the first paragraph. For the formation of glycollic acid, it would be 1.33, for formic acid 2.0 and for oxalic acid 4.0. That formaldehyde under the influence of ultraviolet light of wave-lengths scarcely transmitted by glass acquires the power of reducing copper sulfate in the presence of sodium citrate or carbonate was claimed by Moore and Webster.[9] This assumed photocondensation of formaldehyde (see Chapter 22) did not require the presence of an inorganic activator, probably proceeded at its maximum velocity when the concentration of formaldehyde was approximately 5 per cent and was aided by a slight alkalinity. Ram and Dhar[10] claim to have obtained small yields of reducing sugars when aqueous formaldehyde was exposed to sunlight in the presence of ferric chloride or kieselguhr. In the mixture of sugars (formose) which results from the polymerizing action of certain alkaline condensing agents on formaldehyde, Küster and Schoder[11] have identified *dl*-fructose, a ketopentose and sorbose. Ascorbic acid has been said by West and Ney[12] to be an active catalyst for the formation of reducing sugars from formaldehyde. It is unlikely that a photocondensation of formaldehyde of the type studied in *in vitro* experiments plays a significant role in the processes by which the plant forms sugars and cellulose.

Klein and Werner[13] claim to have detected the production of formaldehyde as an intermediate in assimilation. Other aldehydes have, however, occasionally been suggested as intermediary products in natural photosynthesis.[14] Acetaldehyde has been discussed as such by Klein and Pirschle.[15] Some, like Barton-Wright and Pratt[16] believe the first sugar formed to be a hexose. Parkin,[17] however, believes that the bulk of the hexose sugars detectable in the leaf arise as a result of the inversion of sucrose. Bodnár, Róth and Bernauer[18] believe that, although in the leaves of *Tropaeolum majus,* formaldehyde gives rise to sugars, its presence inhibits the condensation of sugars to starch.

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[5] Shull, C. A., *Science*, **67**, 107 (1928).

[6] von Baeyer, A., *Ber.*, **3**, 68 (1870).

[7] Sabalichschka, T., *Z. Angew. Chem.*, **5**, 684 (1922); *J. Soc. Chem. Ind.*, **42**, 65A (1923).

[8] Willstätter, R., and Stoll, A., *Ber.*, **50**, 1777 (1917).

[9] Moore, B., and Webster, T. A., *Proc. Roy. Soc.*, **90**, 168 (1918); *Chem. Abs.*, **12**, 1992 (1918).

[10] Ram, A., and Dhar, N. R., *J. Indian Chem. Soc.*, **14**, 151 (1937); *Chem. Abs.*, **31**, 7455 (1937).

[11] Küster, W., and Schoder, F., *Z. physiol. Chem.*, **141**, 110 (1924).

[12] West, E. S., and Ney, L. F., *Science*, **84**, 294 (1936).

[13] Klein, G., and Werner, O., *Biochem. Z.*, **68**, 361 (1926).

Attempts to Obtain Photosynthesis Without Chlorophyll. One attack has involved the use of ultraviolet light in the effort to duplicate *in vitro* some of the processes of photosynthesis. Since these attempts have avoided the use of the plant pigments and have employed ultraviolet light of wave-lengths far shorter than those available in sunlight, it is evident that the results can tell but little regarding the occurrences which actually take place in the plant under physiological conditions. If these attempts are viewed in the light of experiments conducted to determine the possibility of artificially producing the carbohydrates as food materials independently of the plant, they afford little hope for a practical outcome. The energy required to produce the carbohydrates which have been claimed in even the most promising of these experiments is far greater than the energy bound in the carbohydrate reaction products.

Baly and Heilbron[19] claimed that detectable quantities of formaldehyde result when an aqueous solution of carbon dioxide is exposed to ultraviolet rays with agitation. The agitation was thought to decrease the local formation of hydrogen peroxide which prevented the possibility of obtaining a formaldehyde test by oxidizing that material to formic acid. In these early experiments it was believed that evidence had been advanced that wave-lengths less than 2200A might produce one or two parts of formaldehyde in 100,000 of carbon dioxide solution in 18 to 72 hours. If wave-lengths of about 2900A were simultaneously used, it was believed that the formaldehyde was polymerized to reducing sugars.

Similar claims had been made previously, although in these, other substances had been employed as catalysts. Moore and Webster[20] claimed to have detected formaldehyde when carbon dioxide solutions containing colloidal uranium oxide were exposed to sunlight, thus confirming still earlier observations of Bach[21] and of Usher and Priestley.[22] Baly and coworkers also claimed to have obtained positive results in visible light by the use of a number of the catalysts of Moore and others, although they were at one time of the opinion that these may have acted instead as internal filters capable of removing those ultraviolet rays which polymerize formaldehyde. Thus this substance might be allowed to accumulate in quantities sufficient for detection. Malachite green, methyl orange, as well as colloidal uranium compounds and ferric hydroxide were, however, believed true catalysts. Baly also emphasized the necessity of controlling the hydrogen ion concentration of the irradiated solutions by maintaining an excess of magnesium carbonate.

[14] Griebel, C, *Z. Unters. Nahr Genussm.,* **48,** 218 (1924).

[15] Klein, G., and Pirschle, K., *Biochem. Z,* **158,** 340 (1926).

[16] Barton-Wright, E. C., and Pratt, M. C., *Biochem. J.,* **24,** 1210, 1217 (1930); see also Klason, P., *Svensk Kem Tids* **46,** 208 (1934), *Chem Abs,* **29,** 2576 (1935); Gordon, R. B, *Ohio J. Sci.,* **29,** 131 (1929); *Chem. Abs.,* **23,** 3951 (1929); Priestley, J. H, *New Phytol.,* **23,** 255 (1924); *Chem. Abs.,* **19,** 3291 (1925).

[17] Parkin, J., *New Phytol.,* **24,** 57 (1925); *Chem. Abs.,* **20,** 3022 (1926).

[18] Bodnár, J., Róth, L. E, and Bernauer, C., *Biochem. Z.,* **190,** 305 (1927); see also Kretovich, V., *Z. physiol. Chem.,* **231,** 265 (1935).

[19] Baly, E. C. C., and Heilbron, I. M., *J Soc Chem. Ind,* **40,** 377 (1921); Baly, E. C. C., Heilbron, I. M., and Barker, W. F, *J. Chem Soc.,* **119,** 1025 (1921); *Nature,* **112,** 323 (1923); Baly, E. C. C., *Ind Eng. Chem.,* **16,** 1018 (1924).

[20] Moore, B., and Webster, T. A, *Proc. Roy Soc,* **B87,** 168 (1913); **B90,** 168 (1918); *Chem. Abs.,* **12,** 1992 (1918).

[21] Bach, A., *Compt. rend.,* **116,** 1145 (1893).

[22] Usher, F. L, and Priestley, J. H, *Proc. Roy. Soc,* **77B,** 369 (1906); **78B,** 322 (1906); Ferrous salts were believed effective by Stoklasa, J., and Zdobnicky, W., *Ber.,* **50,** 1777 (1917); *Centr. Biochem. Biophys.,* **18,** 370.

Many chemists attempted without success to confirm these observations.[23]

During this period, Baly[24] claimed also to have synthesized large amounts of reducing sugars by exposing aqueous 40-per cent formaldehyde solutions to the rays of the quartz mercury arc in the presence of calcium carbonate. By certain concentration methods, there was obtained a viscous syrup with sweet taste and reducing properties. An examination of this material by Irvine and Francis[25] showed no ketoses, polysaccharides or anhydro-sugars, but about 9.3 per cent of sugars and 80 per cent of non-sugar compounds containing hydroxyl groups.

In subsequent work, Baly, Davies, Johnson and Shanassy[26] concluded that the substance first formed from carbon dioxide might be some complex aldehyde other than formaldehyde. They also claimed that complex organic compounds may be synthesized by the action of ultraviolet light on suspensions of various insoluble powders, such as aluminum, barium sulfate, aluminum hydroxide, and basic carbonates of aluminum, magnesium and zinc, in water through which a stream of carbon dioxide is passed. It was thought essential that the carbon dioxide be adsorbed on these materials. The compounds produced appeared to be of the nature of complex carbohydrates. It was also believed[27] that the total amount of material photosynthesized at a colored surface by visible light was greater than that produced at a white surface by ultraviolet light. Nickel or cobalt carbonates were thought particularly effective, although easily poisoned.

Baur and Rebmann,[28] in a repetition of the Moore and Webster experiments were unable to detect formaldehyde, oxalic or glyoxalic acids. Baur and Büchi[29] attributed the formation of carbohydrates in experiments with dyestuffs such as malachite green to a decomposition of the dye rather than to true photosynthesis from carbon dioxide. Their observations were in general confirmed by Dean Burk,[30] who employed condensed sunlight. Nevertheless, the amounts of formaldehyde produced from the dye itself were very small. Amines are also produced, and under aerobic and alkaline conditions, nitrites as well.

Emerson[31] was unable to obtain any photosynthetic effects by the use of a purified nickel carbonate preparation.

Recently, Dhar and Ram[32] claimed that from 100 cc. of a 10-per cent solution of potassium carbonate mixed with one gram of powdered magnesium and in the presence of zinc oxide, gave after 5.5 hours of exposure to direct sunlight 0.0045 gram of formaldehyde, although no reducing sugar could be detected.[33] The occurrence of traces of formaldehyde in rain water was attributed to the action of light of wave-length 2550A, which had escaped absorption by the ozone layer. Decomposition of formaldehyde by the wave-length 2660A is thought to be hindered by the presence of hydrogen in the upper atmosphere.

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[23] Spoehr, H. A., *J. Am. Chem. Soc.*, **45**, 1185 (1923); Porter, C. W., and Ramsperger, H. C., *J. Am. Chem. Soc.*, **47**, 79 (1925); Vorländer, D., *Ber.* **58B**, 2656 (1925); Reggiani, M., *Helv. Chim. Acta*, **15**, 1383 (1932); Qureshi, M., and Mohammad, S. S., *J. Phys. Chem.*, **36**, 2205 (1932); see, however, Dhar, N. R., *J. Chem. Soc.* **124**, 1860 (1923).

[24] See also Pribram, R., and Franke, A., *Ber.*, **44**, 1035 (1911); *Monatsh.*, **33**, 415 (1912); Akhmatov, A. S., and Baruishanskaya-Landsberg, F. S., *J. Phys. Chem. (U.S.S.R.)*, **6**, 83 (1935); *Chem. Abs.*, **29**, 7809 (1935).

[25] Irvine, J. C., and Francis, G. V., *Ind. Eng. Chem.*, **16**, 1019 (1924).

[26] Baly, E. C. C., Davies, J. B., Johnson, M. R., and Shanassy, H., *Proc. Roy. Soc.*, **116A**, 197 (1927); see also Mezzadroli, G., *Rev. ind. agr. Tucumán*, **19**, 154, 526 (1928); *Chem. Abs.*, **23**, 2367 (1929); Mezzadroli, G., and Vareton, E., *Chimie et Industrie*, Special No. 778, March (1931); Mezzadroli, G., and Gardano, G., *Atti acad. Lincei*, **6**, 160 (1927); *Chem. Abs.*, **22**, 760 (1928).

[27] Baly, E. C. C., Stephen, W. E., and Hood, N. R., *Proc. Roy. Soc.*, **116A**, 212 (1927); Baly, E. C. C., *Science*, **68**, 364 (1928); Baly, E. C. C., and Hood, N. R., *Proc. Roy. Soc.*, **122A**, 393 (1929).

[28] Baur, E., and Rebmann, A., *Helv. Chim. Acta*, **5**, 828 (1922).

[29] Baur, E., and Büchi, P. F., *Helv. Chim. Acta*, **6**, 959 (1923).

[30] Burk, D., *J. Am. Chem. Soc.*, **49**, 1819 (1927); *Cf.* Ram, A., [*Proc. Acad. Sci., United Provinces Agra Oudh, India*, **4**, 83 (1934); *Chem. Abs.*, **29**, 7383 (1935); Ram, A., and Dhar, N. R., *J. Indian Chem. Soc.*, **15**, 321 (1938); *Chem. Abs.*, **32**, 8941 (1938)] for the alleged production of formaldehyde from many organic compounds by sunlight.

[31] Emerson, R., *J. Gen. Physiol.*, **13**, 163 (1929); see also Baur, E., *Z. physik. Chem.*, **131**, 143 (1928).

[32] Dhar, N. R., and Ram, A., *Nature*, **129**, 205 (1932); *Z. anorg. allgem. Chem.* **206**, 171 (1932); Rao, G. G., and Dhar, N. R., *J. Phys. Chem.* **35**, 1418, 1424 (1931); Dhar, N. R., and Sanyal, R. P., *Ibid*, **29**, 926 (1925).

[33] Dhar, N. R., and Ram, A., *Nature* **132**, 819 (1933); *J. Indian Chem. Soc.*, **10**, 287 (1933); *Trans. Faraday Soc.*, **30**, 142 (1934); *Nature*, **131**, 800 (1933); *J. Phys. Chem.*, **37**, 525 (1933); Gore, V., *Ibid.*, **39**, 399 (1933).

According to Rajvansi and Dhar,[34] the most effective catalysts for the formation of formaldehyde from carbon dioxide solution in sunlight are manganous chloride and cobalt carbonate, with which a yield of formaldehyde of the order of 0.0005 per cent by volume was claimed. When nascent carbon dioxide was prepared from barium carbonate and hydrogen chloride, formaldehyde was produced by light even in the absence of a photosensitizer. The temperature coefficient of sugar formation in sunlight from a 3-per cent aqueous solution of formaldehyde was found to be 1.2 between 30 and 40°C.

Gore[35] finds that mixtures of tartaric acid and various aldehydes or alcohols in aqueous solutions after exposures to sunlight of 84 or 100 hours without photosensitizers gave positive sugar tests with Benedict's solution. This did not occur in darkness. Gore assumes that light aids the decomposition of tartaric acid by aldehyde to produce nascent carbon dioxide, which reacts with water to produce formaldehyde which polymerizes with the formation of the sugars. It is assumed that when alcohols are used they are first oxidized to aldehydes by light.

Notwithstanding the poor yields that have been reported in all such investigations, Roman[36] patented the production of hexoses and higher carbohydrates by the polymerization of aldehydes, particularly formaldehyde, by light, preferably orange-red. The reaction is said to be best effected in the presence of a compound capable of combining with the carbohydrate, such as an alkaline-earth hydroxide.

In subsequent work, Baly[37] turned to the use of catalysts of ferric oxide supported on kieselguhr previously coated with alumina. The activity was said to be increased by the addition of small quantities of thorium dioxide to the ferric oxide. Bell[38] was unable to confirm these results. Further negative results in the photosynthesis of formaldehyde were also reported by Konstantinova-Shlezinger,[39] and Zscheile[40] reported forty futile attempts to repeat the experiments of Baly with visible light and nickel and cobalt carbonates. He felt that Baly's use of cylinder carbon dioxide may have been a source of organic impurities. Dhar, Rao and Ram[41] claimed success with the use of nickel carbonate and colloidal ferric hydroxide in 2-per cent sodium bicarbonate solutions, notwithstanding Baly's insistence that the catalyst be free from alkali. MacKinney[42] obtained completely negative results with these slightly alkaline catalysts in sunlight or with ultraviolet light between 2900 and 3000A.

Yajnik and Trehana[43] claimed to have verified some of the observations of Baly. White catalysts gave no yield unless artificially colored The best results were claimed for green, red and blue catalysts, copper arsenate being the most efficient of those tested. Baly[44] recently maintained that it is essential for success that there be a surface which is a true crystal lattice of nickel oxide.

THE PHYSIOLOGICAL MECHANISM

Green leaves absorb from 50 to 60 per cent of the incident infrared and approximately 90 per cent of the ultraviolet rays, according to Seybold.[45] In the red region, the maximum absorption by leaves occurs at 6700A. That of an acetone extract of chlorophyll occurs at 6500A. There is a second maximum in the blue-violet, and transmission is greatest in the green. In the living leaf the chlorophyll spectrum is displaced somewhat toward the infrared as compared with that which it exhibits in solution.

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[34] Rajvansi, A. R., and Dhar, N. R., *J. Phys. Chem* , **36**, 567, 575 (1932).

[35] Gore, V., *J. Phys. Chem.*, **37**, 745 (1933)

[36] Roman. L. H.. German P. 590,236, Jan. 4, 1934; *Chem. Abs.*, **28**, 2013 (1934); Carboxyhyd, A.-G British P. 374,044 and 458,359.

[37] Baly, E. C. C., *Nature*, **126**, 666 (1930); *Trans. Faraday Soc.*, **27**, 545 (1931).

[38] Bell, J., *Trans. Faraday Soc.*, **27**, 771 (1931).

[39] Konstantinova-Shlezinger, M., *J. Phys. Chem., U.S.S.R* , **2**, 780 (1931); *Chem. Abs.*, **27**, 5374 (1933).

[40] Zscheile, F. P. Jr., *J. Am. Chem. Soc.*, **54**, 973 (1932).

[41] Dhar, N. R., Rao, G. G., and Ram, A., *Trans. Faraday Soc.*, **27**, 554 (1931); Rao, G. G., and Dhar, N. R , *J. Phys. Chem.*, **35**, 1418 (1931)

[42] MacKinney, G., *J. Am. Chem. Soc.*, **54**, 1688 (1932).

[43] Yajnik, N. A., and Trehana, F. C , *J. chim. phys.*, **28**, 517 (1931).

[44] Baly, E. C. C., *Nature*, **140**, 930 (1937). See also Ostrikov, M. S., *Acta Univ. Voronegiensis*, **9**, No. 3, 95 (1937); *Chem. Abs.*, **32**, 6949 (1938).

[45] Seybold, A., *Planta (Abt. E, Z. wiss. Biol.)*, **21**, 251 (1933); *Chem. Abs.*, **28**, 3758 (1934).

Although the carotenes and xanthophyll also make contributions to the absorption of visible light by the leaf, the absorption of chlorophyll is the predominant cause of the color of the leaf.[46]

That chlorophyll may be separated into fractions was suggested by early observers, and confirmed by Willstätter and Stoll.[47] They showed that there are two green pigments chlorophyll-*a* and chlorophyll-*b* present in all plant leaves and separable by a preferential solubility of chlorophyll-*a* in petroleum ether and of chlorophyll-*b* in 90-per cent methanol. In the higher plants there is about three times as much of the former as of the latter.[48]

Wlodek[49] noted that the stripes of the first absorption band, corresponding to both chlorophyll-*a* and *b*, alter in width during exposure of the leaf to light. This indicates either a change in the relative amounts of the two forms of chlorophyll or the appearance of a new type of spectrum due to unstable compounds of chlorophyll with carbon dioxide. Shifts in the situation of the absorption bands of chlorophyll in the presence of certain hydrophilic and lipophilic materials are considered to support a granular model of the chloroplastid by Wakkie.[50]

Action of Light on Chlorophyll. Crude chlorophyll in alcoholic solution was not decomposed by the action of ultraviolet rays in exposures of five to sixty minutes. Bierry and des Bancels[51] found that on prolonged exposures to two mercury arcs, the solutions became faintly yellow and gave positive tests for urobilinogen. A benzene solution of chlorophyll became colorless under these conditions but did not show the color reactions of urobilinogen.[52] According to Dangeard,[53] when light is allowed to fall on a mixture of chlorophyll and Pinaverdol, the former is decolorized. The latter is also attacked and finally destroyed by the light absorbed, not by itself, but by the chlorophyll. It was suggested that the carotene and xanthophylls which accompany chlorophyll in the leaf might also be similarly bleached by the photosensitizing action of chlorophyll.

Bleaching of chlorophyll occurs in the presence of oxygen and of such acceptors as diethylallyl- and diallylthiocarbamide, according to Weber.[54] Ferrous sulfate is also active in neutral or feebly acid solution. In the absence of an acceptor the rate of bleaching is slow. It increases rapidly in the presence of small amounts of acceptor, attains a maximum and diminishes logarithmically with increasing acceptor concentrations. In all cases there is a marked induction period. The rate of bleaching is but little affected by temperature. The bleaching is greatly inhibited by certain phenols, quinones and amines. It is suggested that on absorption of a photon a molecule of chlorophyll is so activated as to enable it to combine with a molecule of oxygen, forming a peroxide which then oxidizes the chlorophyll. Induction and after effects are attributed to the long life-periods of the intermediate peroxide. With high acceptor concentrations, chlorophyll is stabilized by the reaction: $AO_2+A \rightarrow 2AO$. According to Porret and Rabinowitsch, the reversible bleaching of chlorophyll is proportional to the square root of the light intensity. It is increased by formic acid and suppressed by ferrous chloride.[55]

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[46] The chemistry of chlorophyll has recently been reviewed by Steele, C. C., *Chem. Rev.*, **20**, 1 (1937) and by Fischer, H., *Chem. Rev.*, **20**, 41 (1937).

[47] Willstätter, R., and Stoll, A., "Untersuchungen über Chlorophyll," Berlin, 1913; transl. by Scherz, F., and Merz, A., Science Publishing Co., 1928.

[48] Their photosynthetic functions have been reviewed by Spoehr, H. A., *Annual Rev. Biochem.*, **2**, 453 (1933) and by Stoll, A., *Naturwiss.*, **24**, 53 (1936).

[49] Wlodek, J., *Bull. Internat. Acad. Pol. Sci. Lettres* **B**, 407 (1924); *Chem. Abs.*, **19**, 2687 (1925).

[50] Wakkie, J. G., *Proc. Acad. Sci Amsterdam*, **38**, 1082 (1935); *Chem. Abs.*, **30**, 3024 (1936). Methods for measuring the absorption of radiation by leaves are discussed by Mestre, H., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 191 (1935).

[51] Bierry, H., and des Bancels, J, *Compt. rend.*, **153**, 124 (1911); *J. Chem. Soc.*, **100**, 735 (1911).

[52] See, however, Gouzon, B., *Compt. rend.*, **196**, 1542 (1933).

[53] Dangeard, P. A., *Compt. rend.*, **156**, 1844 (1913).

[54] Weber, K, *Ber.*, **69B**, 1026 (1936); *Nature*, **137**, 870 (1936); Weiss, J., *Nature*, **136**, 794 (1935).

An ethylchlorophyllide solution can be reversibly oxidized by ferric chloride to a yellow unstable intermediary product from which the green solution can be regenerated by reduction with ferrous chloride. The oxidation is greatly favored by illumination.[56]

Hubert[57] notes the possibility of the photodecomposition of chlorophyll during the measurement of its absorption spectrum. Suspensoid particles prepared by injecting an acetone solution of chlorophyll into water bear a negative charge which becomes positive after several hours of exposure to light, owing to photoöxidation.[58] Electrical measurements made with metallic plates coated with chlorophyll and illuminated showed in experiments of Dixon and Poole,[59] that the wave-lengths which are effective in photosynthesis are unable to expel electrons from chlorophyll.

Kögel[60] attributes the photosensitivity of chlorophyll to keto-groups. Roffo[61] finds pure chlorophyll strongly photoactive, a property not shared by xanthophyll, phytosterol, carotene or chlorophyllin.

When a hydrazone of phylloerythrin is exposed to light, its spectrum changes to that of phylloerythrin.[62] Etioporphyrin, exposed to sunlight in the presence of oxygen, forms ethylmethylmaleimide, according to Deželić.[63]

Relation of Chlorophyll to Photosynthesis. The importance of chlorophyll in the photosynthetic process is based upon the agreement between the absorption spectrum of chlorophyll and the effective wave-length regions, and also upon the approximate correlation between the photosynthetic activity of partly etiolated plants and their chlorophyll content. The latter agreement is, however, far from an exact one, so it has been suggested that other internal factors may be involved.[64] Studies at various points in the variegated leaves of Pelargonium by Chapman and Camp[65] revealed that no starch is produced in the non-green parts.

Attempts to reproduce the photosynthetic process *in vitro* by the use of extracts of chlorophyll have not yielded promising results. Osterhout[66] sprinkled a carbon tetrachloride solution of chlorophyll on filter paper in amounts sufficient to give it a deep green color. The treated paper was placed in airtight bell jars with large petri dishes containing 5 cc. of water. Some of the sheets were kept in darkness and others were placed in light for several days until the chlorophyll had bleached to a pale green color. The water in the dishes kept in darkness gave negative aldehyde tests and that in those in the light gave positive tests. Aniline dyes were believed to behave similarly. Baur[67] embedded the chlorophyll in collodion with an oxidation-reduction system such as methylene blue or iron salts and exposed the layer in water to sunlight. Small quantities of formaldehyde could be detected even when the water had been freed from carbon dioxide. The presence of carotene increases the yield. Dolk and van Veen[68] were unable to reduce carbon dioxide by a protein-containing chlorophyll solution, a reaction previously reported by v. Eisler and Portheim.[69]

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[55] Porret, D., and Rabinowitsch, E., *Nature*, **140**, 321 (1937).

[56] Rabinowitsch, E., and Weiss, J., *Nature*, **138**, 1098 (1936).

[57] Hubert, B., *Proc. Acad. Sci. Amsterdam*, **37**, 684 (1934); *Chem. Abs.*, **29**, 1844 (1935).

[58] Bakker, H. A., *Proc Acad. Sci. Amsterdam*, **37**, 688 (1934); *Chem. Abs.*, **29**, 1844 (1935).

[59] Dixon, H. H., and Poole, H. H., *Sci. Proc. Roy. Dublin Soc.*, **16**, 63 (1920); *J. Chem. Soc.*, **118**, II, 343 (1920).

[60] Kögel, G., *Strahlentherapie*, **45**, 587 (1932); *Chem. Abs.*, **27**, 2721 (1933).

[61] Roffo, A. H., *Bol. inst. med. exper. cancer Buenos Aires*, **8**, 68 (1931); *Chem. Abs.*, **26**, 5125 (1932).

[62] Fischer, H., Moldenhauer, O., and Süs, O., *Annalen*, **485**, 1 (1931); *Chem. Abs.*, **25**, 1835 (1931).

[63] Deželić, M., *Bull. soc. chim. roy. Yougoslav*, **6**, 11 (1935); *Chem. Abs.*, **29**, 7998 (1935).

[64] Briggs, G. E., *Proc. Roy. Soc.*, **91B**, 249 (1920).

[65] Chapman, A. G., and Camp., W. H., *Ohio J. Sci.* **32**, 197 (1932); *Chem. Abs.*, **26**, 4629 (1932).

[66] Osterhout, W. J. V., *Am. J. Botany*, **5**, 105, 511 (1918); Osterhout, W. J. V., and Haas, A. R. S., *Science*, **47**, 420 (1918).

In the case of *Pinus Strobus* and *Picea excelsa,* Burns[70] finds wave-length limits for photosynthesis to be 7400 to 4500A approximately. Ursprung[71] found starch formation possible between 7600 and 3300A. Both the red and the blue-violet regions are regarded as necessary for normal photosynthetic activity by Dastur and Mehta.[72] On the basis of equal incident energies at various wave-lengths, Hoover[73] found the entire visible spectrum between 7200-7500A and less than 3650A to be effective. A principal maximum occurred at 6550A in the red and a secondary one at 4400A in the blue. Greater reflection and transmission in the green diminished the effectiveness of these rays. Harder, Döring and Simonis suggest that the assimilatory apparatus of green plants may be able to adapt itself to the wave-length of light in which it is grown.[74]

A new type of starch formation under the influence of wave-lengths shorter than 3000A has been discussed by Richter,[75] who postulates the existence of a chlorophyllase in the leaf to account for his results.

The Mode of Action of Chlorophyll in Photosynthesis. The investigation of the mechanism of the reaction is unfortunately complicated by the necessity for studying it as it occurs in living tissues. Fundamental investigations of the process in leaves were made by Blackman[76] in 1905. These led to a recognition that the rate of the process as conducted under different conditions may be limited by different factors.

Thus, Hoover, Johnston and Brackett[77] find that in wheat, carbon dioxide limits the rate when high light intensities are used, although under conditions of high carbon dioxide concentration, light becomes the limiting factor. In an extensive transition range, both factors may be limiting, in consequence of the wide variation in the illumination and carbon dioxide concentration available for different chloroplasts. Blackman had also called attention to the influence of temperature in altering the nature of the photosynthetic processes.[78] The temperature of the leaf also alters transpiration, and changes the state of the plasma, alters the ease of penetration of the gases and may have other effects. Furthermore, respiration is also occurring and its effects upon the results require consideration. Dhar[79] suggests that an increase in temperature may affect the respiration more than the photosynthetic process. Another complicating factor is the possibility of the existence of enzymes, which may in some manner be concerned in the process.[80] Various methods of killing leaves affect the photosynthetic process about as do various methods of inactivating enzymes. Inman[81] believes some light-sensitive substance contributes to the production of free oxygen in living but not in dead, plant cell tissues. It is inactivated by trypsin, but not by pepsin, erepsin, amylopsin, diastase, urease or papain. The maximum evolution of oxygen is obtained between pH 5 and 6. The critical temperature for its evolution is 55°C, regardless of pH; that for catalase is 70°C. Wurmser[82] directed attention to the influence of alterations of the cellular reduction potential upon the process. Rhythms in the production and disappearance of starch during 24-hour periods have been observed by Stănescu,[83] who followed quantitatively the variations in the products in the leaves of green plants during the course of a day. The water content of the leaves also exerts a great influence upon the rate of the process.[84] Wood[85] showed that the injection of water into a cherry-laurel leaf lowers its rate of assimilation until nearly all the injected water has disappeared from the intercellular spaces. Dehydration of the leaf by a dry wind[86] retards photosynthesis. Still another factor is the amount of carbohydrate already present.[87]

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[67] Baur, E., *Helv Chim. Acta,* **18,** 1157 (1935); **20,** 387, 391, 398 (1937).

[68] Dolk, H. E., and van Veen, A. G., *Biochem. Z.,* **185,** 165 (1927).

[69] v. Eisler, M., and Portheim, L., *Biochem. Z.,* **135,** 293 (1923).

[70] Burns, G. R., *Science,* **78,** 130 (1933); *Plant Physiol.,* **8,** 247 (1933); **9,** 645 (1934); *J. Am. Chem. Soc.,* **59,** 944 (1937), *Am. J Botany,* **24,** 257 (1937); *Vt. Agr. Expt. Sta., Bull.* **402,** 2 (1936); *Chem. Abs.,* **31,** 4699, 5020 (1937), *Am. J. Botany,* **25,** 166 (1938).

[71] Ursprung, A., *Ber. deut. botan. Ges.,* **35,** 44 (1917).

[72] Dastur, R. H., and Mehta, R. J., *Ann. Botan.,* **49,** 809 (1935); *Chem. Abs.,* **30,** 503 (1936); see also Dastur, R H., and Samant, K. M , *Ann. Botan.,* **47,** 295 (1933); *Chem. Abs.,* **27,** 4270 (1933), Dastur, R. H., and Solomon, S., *Ann. Botan.,* **1,** 147 (1937); *Chem. Abs.,* **31,** 2639 (1937).

[73] Hoover, W. H., *Smithsonian Inst. Miscellaneous Collections,* **95,** No. 21 (1937). No increased action due to the joint action of all wave-lengths of white light over that due to the sum of their individual effects occurs, according to Montfort, C., *Ber. deutsch. botan. Ges.,* **55,** 142 (1937); *Chem. Abs.,* **31,** 7089 (1937). An opposite result is noted by Danilov, A. N., *Arch. sci. biol. (U S.S.R.),* **43,** Nos. 2-3, 365 (1936); *Chem. Abs.,* **32,** 6694 (1938).

[74] Harder, R., Döring, B., and Simonis, W., *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse Fach Gruppe,* **VI, 2,** 129 (1936); *Chem Abs.,* **32,** 7958 (1938).

[75] Richter, O., *Sitzber. Akad. Wiss. Wien, Math. naturw. Kl.,* I, **144,** 157 (1935); *Chem. Abs.,* **31,** 3762 (1937).

[76] Blackman, F. F., *Proc. Roy. Soc.,* **76B,** 402 (1905); *Ann. Botan.,* **19,** 28 (1905).

[77] Hoover, W. H., Johnston, E. S., and Brackett, F S., *Smithsonian Miscellaneous Collections,* **87,** 16 (1933); see also Smith, E. L., *J. Gen. Physiol.,* **22,** 21 (1938).

To avoid so far as possible these many complicating factors some of the investigations which have proved most significant in the interpretation of the mechanism of the process have been conducted on the algae. Warburg and Negelein[88] made a series of observations of the energy exchange in the stems of *Chlorella* using light of four spectral regions. In general the reaction yield decreased with decreasing wave-length, but no relation could be discerned between the yield and the absorption coefficients. The yield in the red, a region of high absorption, was greater than that in the green, a region of very weak absorption, but the yield in the latter case was greater than that in the blue, the region of strongest absorption. The decomposition in the ultraviolet and in the region between 7000 and 7800A could not be accurately determined. There was no utilization of carbon dioxide under the influence of light in the infrared. In *Ulva lactuca*, the yield for equal incident intensities was a maximum in the region in which the chlorophyll absorption was least, according to Wurmser.[89]

Warburg recognized the need for the absorption of several quanta per molecule in order to secure enough energy for the reaction to proceed. The results indicated that four quanta of red or yellow light or five of blue light were required for the decomposition of a molecule of carbon dioxide. When corrections were made for the light absorbed by the other photochemically inactive pigments present, it was found that more than three and less than five quanta of blue light were required per molecule of carbon dioxide. The energy efficiency of the total reaction, obtained by dividing 112 kcal. by four times the equivalent energy of the light employed, was found to be 65 per cent for 6600A, 57 per cent for 5780A and 43 per cent for 4360A.

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[78] Chesnokov, V., and Bazuirina, E. N., *Compt rend. acad. sci. U.R.S.S.*, **8**, 193 (1930A); *Chem. Abs.*, **25**, 313, 2457 (1931). A review in Russian is given by Nekrasov, N. I., and Krashennikov, F. N., *Uspekhi Khim.*, **6**, 334 (1937).

[79] Dhar, N. R., *J. Indian Chem. Soc.*, **10**, 541 (1933); *Chem. Abs.*, **28**, 2293 (1934); Singh, B N., and Kumar, K., [*Proc. Indian Acad. Sci.*, **1B**, 736 (1935); *Chem. Abs.*, **29**, 6277 (1935)] consider the effects of temperature on the process in radish leaves.

[80] Molisch, H., cited by Stiles, W., *Scientia*, **41**, 122 (1927); Molisch, H., *Z. Botan.*, **17**, 577 (1925).

[81] Inman, O. L., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 184 (1935); *Chem. Abs.*, **30**, 7627 (1936).

[82] Wurmser, R., *Compt. rend soc. biol.*, **95**, 1237 (1926).

[83] Stănescu, P. P., *Ann. Sci. Univ. Jassy*, **14**, 383 (1927); *Chem. Abs.*, **22**, 2390 (1928).

[84] Dastur, R. H., *Ann. Botan.*, **39**, 769 (1925).

[85] Wood, J. G., *Australian J. Exp. Biol*, **6**, 127 (1929); *Chem. Abs.*, **24**, 1882 (1930).

[86] Skvortzov, S. S., *Bull. Applied Bot., Gen. Plant Breeding, Leningrad*, **25**, No. 3, 45 (1931); *Chem. Abs.*, **26**, 5605 (1932).

[87] Kursanov, A. L., *Planta, Abt. E. Z. wiss. Biol.*, **20**, 535 (1933); *Chem Abs.*, **28**, 2750 (1934); Spoehr, H. A., and Long, F. L, *Carnegie Inst Washington, Yearbook*, 17, 60 (1918); Lyubimenko, V. N., *Rev. Gen. Botan.*, **40**, 415, 486 (1928); *Chem. Abs.*, **23**, 412 (1929) .

[88] Warburg, O., and Negelein, E., *Z. physik. Chem.*, **106**, 191 (1923).

[89] Wurmser, R., *Compt. rend.*, **177**, 644 (1923); *J. Phys. Radium*, **7**, 33 (1926). The work indicated that Einstein's law did not directly account for the photosynthetic behavior of this sea-weed.

It was also shown in later experiments conducted at very high and at very low light intensities that it is possible to distinguish between the photochemical reaction with low temperature coefficient and a subsequent reaction, called by Warburg the Blackman reaction. This has a higher temperature coefficient and is a thermal reaction.[90] For a given wave-length, the specific photochemical reaction is greater the smaller the intensity, and with very low intensities the action is proportional to the intensity.

Narcotics, such as 0.5×10^{-4} molar phenylurethane, powerfully inhibited both the photochemical and the Blackman reactions. Hydrogen cyanide and hydrogen sulfide, however, inhibited only the Blackman reaction.

Considerable information has been yielded by studies of the effect of intermittent light. By using a rotating sector, Brown and Escombe[91] found that three-quarters of the light from a given source could be cut out in each revolution of the sector without decreasing the rate of photosynthesis by leaves. Willstätter attributed this to the slowness of the diffusion of carbon dioxide to the cells during the dark period. In Warburg's experiments with light of high intensity and with a high concentration of carbon dioxide, it was found that even in algae, a given amount of light reduced more carbon dioxide when applied intermittently than when the illumination was continuous. The increase in the yield depended upon the frequency of the flashing. It was 10 per cent with four periods per minute and 100 per cent with a frequency of 8000 per minute. Emerson and Arnold[92] believed that certain steps in the Blackman reaction proceed during the dark period. When the light intensity is high, the initial photochemical reaction is capable of proceeding at great speed. In continuous light, however, it can go no faster than the Blackman reaction. Since it seemed likely that in the latter, chlorophyll is regenerated, it may be that the Blackman reaction limits the rate of the photochemical process. Higher efficiency of utilization of the light would be obtained if each flash lasted only long enough to build up the equilibrium concentration of intermediate products and each dark period were long enough to allow the slower Blackman reaction time to use up all the intermediate products present at the end of the light period. By using only fifty flashes per second and making the flashes much shorter than the dark periods, Emerson and Arnold were able to increase the yield by 300 to 400 per cent of that under continuous illumination. The necessary dark period varied from about 0.03 to 0.4 second, depending on the temperature. The light period could be reduced to 0.00001 second. The light reaction is dependent upon the carbon dioxide concentration and is inhibited by narcotics. They differed from Warburg in not finding the dark reaction inhibited by narcotics, although it is inhibited by cyanides. It is independent of the carbon dioxide concentration. From the speed of the light reaction, it was suggested that a chlorophyll-carbon dioxide complex may be activated to form molecules capable of undergoing the Blackman reaction.

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[90] Warburg, O., *Biochem. Z.*, **166**, 386 (1925); **100**, 230 (1919); **103**, 188 (1920).

[91] Brown, H. T., and Escombe, F., *Proc. Roy. Soc.*, **76B**, 29 (1905). For reviews, see Briggs, G. E., *Biol. Review Cambridge Phil. Soc.*, **10**, 460 (1935); Emerson, R., *Enzymforsch.*, **5**, 305 (1936).

[92] Emerson, R., and Arnold, W., *J. Gen. Physiol.*, **15**, 391 (1931-2); **12**, 623 (1929). There is no similarity between the Blackman reaction and the decomposition of hydrogen peroxide by *Chlorella*, according to Emerson, R., and Green, L., *Plant Physiol.*, **12**, 537 (1937).

From studies on several higher plants, Briggs[93] concluded that, contrary to the results of Warburg and Negelein, the number of quanta required for the production of a molecule of carbon dioxide increases discontinuously with increasing wave-length. In the case of spruce, Burns[94] found the relative number of quanta required per molecule of carbon dioxide to be 9.5, 10 and 5 for the wave-length regions 7200-6300A, 7200-5600A and 4700-3900A. Thus the quantum yields were much smaller than those found by Warburg. Recently, Manning, Stauffer, Duggar and Daniels[95] reported that an extensive series of investigations had failed to confirm the quantum yield for *Chlorella* reported by Warburg as 0.25. Instead, the value was much lower, 0.05, and in some experiments, particularly those with higher light intensities, was still lower, even approximating zero. No explanation of the discrepancy could be advanced. It was pointed out that the Warburg results indicated a high enough efficiency in the utilization of the energy[96] for it to be profitable to attempt formulations of the mechanism of the coupled reactions which occur. The newer low quantum yields, however, make possible a large number of conceivable mechanisms, and leave our knowledge of the nature of this fundamental reaction in a chaotic state. Only a brief discussion will, therefore, be given of a few of the mechanisms which have been suggested.[97]

The mechanism suggested by Willstätter and Stoll was based upon their belief that carbon dioxide reacts with chlorophyll-*a* to form a carbon dioxide-chlorophyll complex of the same color as chlorophyll.[98] The absorption of light was thought to convert this into an isomer of peroxide-like nature. This is capable of liberating oxygen and an oxymethylene group with regeneration of chlorophyll.[99] Several observations by Warburg lent support to this theory. *Chlorella* in 0.03 molar hydrogen peroxide solution in darkness evolved the same amount of oxygen as does the same amount of the irradiated algae in the Blackman reaction. The effects of temperature, hydrogen cyanide and narcotics on the Blackman reaction and the evolution of oxygen from hydrogen peroxide by *Chlorella* were similar.

Photosynthesis occurs in the absence of oxygen in at least 14 species of marine algae. Within a second of the illumination, oxygen is liberated and may be detected by its action on luminous bacteria.[100] This is confirmed by Gaffron.[101] Carbon monoxide influences the process, possibly by an action on an enzyme assumed to control the liberation of oxygen in the Blackman reaction. Kohn[102] finds that iodoacetic acid and its amide inhibit photosynthesis by attacking the Blackman reaction.

Ostwald[103] suggested the possibility of a primary photoactivation to a lipoid peroxide at an interface between lipoid and protein, the assumed reaction being in some manner promoted by chlorophyll, which was not thought to enter directly into the mechanism.

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[93] Briggs, G. E., *Proc. Roy. Soc.*, **105B**, 1 (1929); *Brit. Chem. Abs.* **A**, 960 (1929).

[94] Burns, G. R., *Plant Physiol.*, **8**, 247 (1933); *Chem Abs.*, **27**, 3239 (1933).

[95] Manning, W. M., Stauffer, J. F., Duggar, B. M., and Daniels, F., *J. Am. Chem. Soc.*, **60**, 266 (1938); Manning, W. M., Juday, C., and Wolf, M, *ibid.*, 274; *Trans. Wis. Acad. Sci.* **31**, 377 (1938).

[96] Adams, E. Q., interprets the results as indicating an efficiency of 98.6 per cent [*J. Am. Chem. Soc.*, **48**, 292 (1926)] if the fundamental reaction is assumed to be $CO_2 + 3H_2O \rightarrow HCHO + 2H_2O_2$.

[97] Pfeilsticker, K., *Biochem. Z.*, **199**, 12 (1928) applied stereochemical ideas to the theory of photosynthesis.

[98] Willstätter, R., and Stoll, A., *Ber.*, **50**, 1791 (1917); see also Peklo, J., *Chem. News*, **129**, 90 (1924).

[99] An earlier theory of Willstätter, since discarded, assumed a participation of xanthophyll and carotene. See also Heilbron, I. M., *J. Soc. Chem. Ind.*, **43**, 89T (1924); *Chem. Abs.*, **15**, 3072 (1921).

[100] Harvey, E. N., *Plant Physiol.*, **3**, 85 (1928); *Chem. Abs.*, **23**, 185 (1929).

[101] Gaffron, H., *Biochem, Z.*, **280**, 337 (1935).

[102] Kohn, H. I., *J. Gen. Physiol.*, **19**, 23 (1935).

[103] Ostwald, Wo., *Kolloid Z.*, **33**, 356 (1923).

Attention was also devoted to the possibility that light enables the chlorophyll in some manner to split hydrogen from water, producing hydrogen peroxide. Thunberg[104] suggested that hydrogen, carbon dioxide and water might react to produce oxygen and H_4CO_2, the latter breaking down to formaldehyde and water. Weigert[105] suggested that in an internal photoelectric effect in a chlorophyll-water complex, the passage of an electron from the pigment to the water with the production of a hydrogen atom and hydroxyl ion may occur. Two hydroxyl ions might then form hydrogen peroxide, returning the electrons to chlorophyll molecules.

Shibata and Yakushiji[106] suggest that the chlorophyll-carbonic acid complex binds four water molecules coördinatively to the magnesium atom. The absorption of four quanta activates the water molecules of the complex forming four hydrogen atoms and four hydroxyl groups. The hydrogen atoms react with carbonic acid with the formation of formaldehyde and two molecules of water. The four hydroxyl radicals form two molecules of hydrogen peroxide which are subsequently decomposed to water and oxygen by the leaf catalase. The catalase poison, hydroxylamine, added in low concentrations, inhibits the liberation of oxygen and changes assimilation into respiration. This theory was developed particularly to account for the now disputed quantum yield of 0.25.

Kögel[107] believed that chlorophyll activates the carbon dioxide and forms $(OH)_2C(OH)_2$ as the initial product.

Kautsky and Hirsch[108] studied the changes in the fluorescence of chlorophyll in leaves during exposure to light. The intensity of the fluorescence rises rapidly to a maximum (one second) and then slowly drops (four minutes) to a low value, which thereafter remains constant. At O°C., or after the addition of hydrogen cyanide, the initial rise still occurs but there is no subsequent decrease. It is suggested that the period of falling fluorescence intensity represents an induction period during which the Blackman reaction occurs. Normal assimilation is assumed to occur on the final weak fluorescent level of the curve for the fluorescence intensity at various times during irradiation. The steep initial rise in the curve, which is independent of temperature or cyanide, increases with the light intensity. It is ascribed to the establishment of the photochemical equilibrium:

Chlorophyll-$CO_2 + h\nu \rightleftarrows$ Chlorophyll-formaldehyde peroxide. The fluorescence is largely inhibited by oxygen.[109] The absorption of a quantum by the pigment system[110] activates it so that it fluoresces intensely. The fluorescence may then be quenched by the transfer of the excitation energy to an unidentified compound containing loosely bound molecular oxygen, designated $A(O_2)$. This energy (about 37 kcal. or a little less than the red fluorescence, 42 kcal.) stabilizes the oxygen compound. The energy-transfer is a surface phenomenon, which can be abolished by such a surface-active substance as phenylurethane. The stable excited oxygen compound is changed back to the dissociable one in the chloroplasts by a heavy metal catalyst, liberating oxygen, energy and the substance A. The latter again combines with molecular oxygen. It is this reaction which depends upon temperature and which is inhibited by cyanides. The energy liberated in the breakdown of the oxygen compound is utilized in the reduction of carbon dioxide.

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[104] Thunberg, T., *Z physik Chem*, **106**, 305 (1923). A substance liberating iodine from potassium iodide is said to be formed when leaves of sugar cane (also stalks and roots) are exposed to sunlight Fujii, M., and Nishioeda, M., *Rept. Gov. Sugar Expt. Sta., Tainan, Formosa*, No. 5, 47 (1938); *Chem. Abs.*, **32**, 8487 (1938).

[105] Weigert, F., *Z. physik. Chem.*, **106**, 313 (1923).

[106] Shibata, K., and Yakushiji, E, *Naturwiss*, **21**, 267 (1933); Yakushiji, E, *Acta Phytochim.*, **7**, 93 (1933); *Chem. Abs.*, **27**, 4269 (1933).

[107] Kögel, G., *Naturwiss.*, **19**, 571 (1931).

[108] Kautsky, H, and Hirsch, A., *Naturwiss*, **19**, 964 (1931); Kautsky, H, and Spohn, H., *Biochem. Z*, **274**, 435 (1934); **277**, 250 (1935).

[109] Kautsky, H, Hirsch, A., and Davidshofer, F., *Ber.*, **65**, 1762 (1932); *Chem. Abs*, **27**, 1029 (1933), Dastur, R. H., and Desai, B. L., [*Annal. Botan*, **47**, 69 (1933)] interpret the curves for fluorescence on the basis of a double photo-reaction involving, first the activation of carbon dioxide and second, the decomposition of water.

[110] Kautsky, H., and Hirsch, A., *Biochem. Z.*, **274**, 423 (1934). For recent studies of fluorescence in *Chlorella*, see Wassink, E. C., Vermeulen, D., Reman, G. H., and Katz, E., *Enzymologia*, **5**, 100, 110 (1938).

That the dehydrogenation of chlorophyll may play a part in the photosynthetic process was suggested by Conant, Dietz and Kamerling.[111] In a dark enzymatic process, six molecules of carbon dioxide may remove two hydrogen atoms from each of twelve chlorophyll molecules forming a hexose, six molecules of water and twelve of dehydrochlorophyll. In a subsequent photochemical reaction, chlorophyll is regenerated by abstracting hydrogen from water, releasing its oxygen.

On the basis of some observations by Stoll,[112] Willstätter [113] altered the Conant concept of the process. In place of assuming that the hydrogen atoms of chlorophyll are lost as a pair in its dehydrogenation, he considered them to transfer separately, monodehydrochlorophyll thus acting as an intermediary compound. It is formed by the action of an oxygen molecule upon chlorophyll and is converted into dehydrochlorophyll by the transfer of its hydrogen atom to the magnesium carbonic acid complex. Then, in light, the dehydrochlorophyll, acting with water, reforms monodehydrochlorophyll and the hydroxyl radical. The former then again transfers its hydrogen to the magnesium-carbonic acid complex and the resulting dehydrochlorophyll again absorbs light. After the transfer of four hydrogen atoms to the magnesium complex with carbonic acid, the dehydro- and monodehydro-compounds are reconverted into chlorophyll by the light reaction and by a reaction in which water and monodehydrochlorophyll form the hydroxyl radical and chlorophyll.

Franck[114] believed that the Willstätter mechanism, with monodehydrochlorophyll as the significant compound, could be altered slightly to correspond to the energy yields of the reaction and with the data of the Kautsky fluorescence curves. The initial rise in the Kautsky curve corresponds to a photo-process in which hydrogenated chlorophyll gives monodehydrochlorophyll and atomic hydrogen, the latter reacting with oxygen and water to give hydrogen dioxide. The photochemical yield of this reaction is poor. The subsequent drop in the fluorescence corresponds to a process in which monodehydrochlorophyll reacts with carbon dioxide with the production of hydroxychlorophyll and formic acid. In subsequent reactions in light, monodehydrochlorophyll, formaldehyde and hydrogen peroxide are produced. During the slow dark reaction, the original hydrogenated chlorophyll is reformed. It will be noted that the Franck theory assumes a photo-dissociation of a lightly bound hydrogen atom from chlorophyll. The recombination of this hydrogen atom produces a chemiluminescence of the same color as that of the fluorescence. It is, therefore, possible to determine from the fluorescence wave-length limits the energy required for the separation of the hydrogen atom. From the long wave-length limit of the narrow fluorescent band at 6800A, this is concluded to be 41.4 kcal.

The reactions of the Franck preparatory photoprocesses are written:

$$(1) \qquad \text{HH—Chlorophyll} + h\nu \longrightarrow \text{H-Chlorophyll} + \text{H}.$$

$$(2) \qquad H + O_2 \longrightarrow O_2H$$

$$(3) \qquad O_2H + H_2O \longrightarrow H_2O_2 + OH$$

$$(4) \qquad OH + OH \longrightarrow H_2O_2.$$

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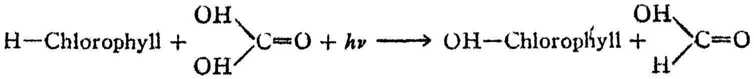
[111] Conant, J. B., Dietz, E. M., and Kamerling, S. E., *Science*, 73, 268 (1931)

[112] Stoll, A., *Naturwiss.*, 20, 955 (1932).

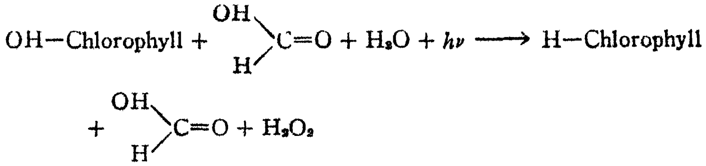
[113] Willstätter, R., *Naturwiss.*, 21, 252 (1933).

[114] Franck, J., *Naturwiss.*, 23, 226 (1935); *Chem. Rev.*, 17, 443 (1935).

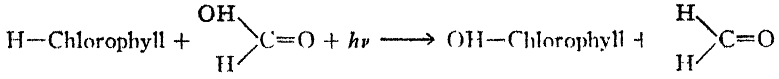
The equations for the assimilation process proper are written:

(1) 

$$\text{H—Chlorophyll} + \begin{matrix}\text{OH}\\ \text{OH}\end{matrix}\!\!>\!\text{C=O} + h\nu \longrightarrow \text{OH—Chlorophyll} + \begin{matrix}\text{OH}\\ \text{H}\end{matrix}\!\!>\!\text{C=O}$$

(2) 

$$\text{OH—Chlorophyll} + \begin{matrix}\text{OH}\\ \text{H}\end{matrix}\!\!>\!\text{C=O} + H_2O + h\nu \longrightarrow \text{H—Chlorophyll} + \begin{matrix}\text{OH}\\ \text{H}\end{matrix}\!\!>\!\text{C=O} + H_2O_2$$

(3) 

$$\text{H—Chlorophyll} + \begin{matrix}\text{OH}\\ \text{H}\end{matrix}\!\!>\!\text{C=O} + h\nu \longrightarrow \text{OH—Chlorophyll} + \begin{matrix}\text{H}\\ \text{H}\end{matrix}\!\!>\!\text{C=O}$$

(4) $\text{OH—Chlorophyll} + H_2O + h\nu \longrightarrow \text{H—Chlorophyll} + H_2O_2$.

These equations were held to be energetically possible. In (1) and (3), light causes a change in position of an hydroxyl group of the bound carbonic or formic acid with a hydrogen atom of chlorophyll. In each case the hydrogen atom is the more firmly bound.

As to the possibility of reactions (2) and (4) it is said that it is necessary to supply enough energy to dissociate water into H and OH and in addition to separate the OH from the chlorophyll residue. The former requires 115 kcal. and the latter about 20 kcal., assuming the hydroxyl group to be at most half as firmly bound as the hydrogen on chlorophyll. There are available 41 kcal. by absorption of a quantum, and the same amount by the binding of a hydrogen atom on the chlorophyll residue and finally 52 kcal. from the combination of two hydroxyl groups to hydrogen peroxide. The new feature in the Franck formulation is the production of the more loosely bound OH-chlorophyll; this was believed to overcome the energetic difficulties in the previous formulation of the mechanism by Willstätter.

Oxygen is assumed necessary only for the preparatory processes. In its absence, irradiation would lead to the production of some carbon dioxide and the strongly fluorescent dehydrochlorophyll. This was believed to lose its energy by fluorescence most readily. This was held to explain the Kautsky curves in the absence of oxygen in which the fluorescence rose rapidly to a maximum after which it remained constant. Kautsky,[115] however, states that his curve of this type was obtained in the presence of small amounts of oxygen, but not in its absence. When oxygen was absent, he could observe no fluorescence. Moreover, Kautsky maintains that his conception of the processes is in agreement with the work of Warburg on the separation of the process into a photochemical one and the Blackman reaction.

The study of fluorescence spectra has been extended to that of pheophorbide-*b* by Knorr and Albers,[116] who follow its change during irradiation in the presence of various gases, oxygen, nitrogen and carbon dioxide.

Wohl[117] shows that the energy of four quanta of 6800A, light which still gives photosynthesis, is smaller than the energy difference between the initial and final products of the overall reaction for the Franck mechanism, 192 kcal. At 6600A four quanta give 172 kcal. Franck and Herzfeld[118] suggest that for such a fluorescent, polyatomic molecule as chlorophyll, which has many degrees of freedom, the missing 20 kcal. may be supplied from the thermal energy. Franck has subsequently altered his suggested mechanism.[119] The preparatory reaction was shown unnecessary by Gaffron.[120] The assumption of hydrogen peroxide is avoided in Franck's most recent mechanism. The chlorophyll-carbonic acid complex is assumed to be attached to an organic molecule ROH. The absorption of a quantum is thought to convert this into a peracid.

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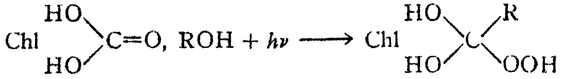
[115] Kautsky, H., *Naturwiss.*, **23**, 389 (1935); Kautsky, H., and Flesch, W., *Biochem. Z.*, **284**, 412 (1936); Kautsky, H., and Marx, A., *Naturwiss.*, **24**, 317 (1936); *Biochem. Z.*, **290**, 248 (1937); Kautsky, H., and Hormuth, R., *Naturwiss.*, **24**, 650 (1936); *Biochem. Z.*, **291**, 285 (1937); Kautsky, H., *Ibid.*, **291**, 271 (1937).

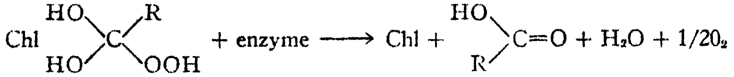
[116] Knorr, H. V., and Albers, V. M., *Phys. Rev.*, **47**, 329 (1935); *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 87, 98 (1935).

[117] Wohl, K., *Z. physik. Chem.*, **31B**, 152 (1935); see also Gaffron, H., and Wohl, K., *Naturwiss.*, **24**, 81, 103 (1936).



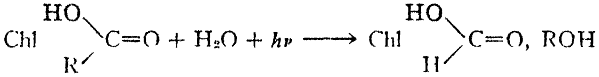
$$\mathrm{Chl}\ {}^{\mathrm{HO}}_{\mathrm{HO}}{>}\mathrm{C{=}O,\ ROH} + h\nu \longrightarrow \mathrm{Chl}\ {}^{\mathrm{HO}}_{\mathrm{HO}}{>}\mathrm{C}{<}^{\mathrm{R}}_{\mathrm{OOH}} \qquad (1)$$

In a thermal enzyme reaction, this peracid is converted into an acid with liberation of oxygen.



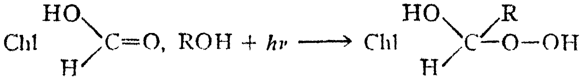
$$\mathrm{Chl}\ {}^{\mathrm{HO}}_{\mathrm{HO}}{>}\mathrm{C}{<}^{\mathrm{R}}_{\mathrm{OOH}} + \text{enzyme} \longrightarrow \mathrm{Chl} + {}^{\mathrm{HO}}_{\mathrm{R}}{>}\mathrm{C{=}O} + \mathrm{H_2O} + 1/2\mathrm{O_2} \qquad (1a)$$

Absorption of another quantum produces formic acid.



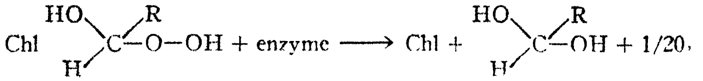
$$\mathrm{Chl}\ {}^{\mathrm{HO}}_{\mathrm{R}}{>}\mathrm{C{=}O} + \mathrm{H_2O} + h\nu \longrightarrow \mathrm{Chl}\ {}^{\mathrm{HO}}_{\mathrm{H}}{>}\mathrm{C{=}O,\ ROH} \qquad (2)$$

This in turn on absorption of a quantum produces a peraldehyde



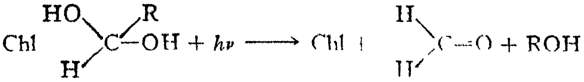
$$\mathrm{Chl}\ {}^{\mathrm{HO}}_{\mathrm{H}}{>}\mathrm{C{=}O,\ ROH} + h\nu \longrightarrow \mathrm{Chl}\ {}^{\mathrm{HO}}_{\mathrm{H}}{>}\overset{\mathrm{R}}{\mathrm{C}}\mathrm{{-}O{-}OH} \qquad (3)$$

which may then liberate oxygen in a thermal enzyme process.



$$\mathrm{Chl}\ {}^{\mathrm{HO}}_{\mathrm{H}}{>}\overset{\mathrm{R}}{\mathrm{C}}\mathrm{{-}O{-}OH} + \text{enzyme} \longrightarrow \mathrm{Chl} + {}^{\mathrm{HO}}_{\mathrm{H}}{>}\overset{\mathrm{R}}{\mathrm{C}}\mathrm{{-}OH} + 1/2\mathrm{O_2} \qquad (3a)$$

The aldehyde on absorption of a quantum may then produce formaldehyde.



$$\mathrm{Chl}\ {}^{\mathrm{HO}}_{\mathrm{H}}{>}\overset{\mathrm{R}}{\mathrm{C}}\mathrm{{-}OH} + h\nu \longrightarrow \mathrm{Chl} + {}^{\mathrm{H}}_{\mathrm{H}}{>}\mathrm{C{=}O} + \mathrm{ROH} \qquad (4)$$

It is not possible in a limited space to discuss the mathematical developments of these reactions made by Franck, and their application to the rapidly accumulating body of experimental data. Gaffron suggests that a free-moving enzyme of the Blackman reaction forms in the dark an inactive dissociable oxygen compound. The complex can be activated by excess light energy when in a reducing location. He believes this may explain the observed rapid oxygen consumption directly after intensive illumination, and the high temperature coefficient of the induction.[121]

Wohl gives reasons for believing the Franck and Herzfeld reaction chain mechanism kinetically impossible.[122] It is recently suggested by Baas-Becking and Hanson [123] that in the chloroplast the chlorophyll molecules occur in planes and are oriented in tetrads with the pentanon ring of each pointing to the same center, and that orthocarbonic acid is fixed at this center by the active hydrogen atoms of the four chlorophyll molecules.

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[118] Franck, J., and Herzfeld, K. F., *J. Phys. Chem.*, **41**, 97 (1937); Franck, J., *J. Wash. Acad. Sci.*, **27**, 317 (1937).

[119] Franck, J., and Herzfeld, K F, *J. Chem Physics*, **5**, 237 (1937)

[120] Gaffron, H., *Naturwiss.*, **23**, 528 (1935).

[121] Gaffron, H., *Naturwiss.*, **25**, 460 (1937); *Chem. Abs.*, **31**, 8557 (1937); *Naturwiss.*, **25**, 715 (1937); *Chem Abs.*, **32**, 2977 (1931).

Knoll, Matthews and Crist regard the Blackman reaction as an enzymatic decomposition of a peroxide formed in the photo-process. They find it the rate-determining process in the oxygen evolution at high light intensities and high carbon dioxide concentrations.[124]

Because of their highly controversial and speculative nature, further consideration of the details of theories of the photosynthetic mechanism must be left to the specialist in this most important field.

Photosynthetic Units. In intermittent light experiments on cells with varied chlorophyll content, Emerson and Arnold [125] showed that for every 2480 molecules of chlorophyll one molecule of carbon dioxide was reduced in a single flash. This means either that the quantum efficiency is very low or that most of the light is absorbed by chlorophyll molecules not in contact with carbon dioxide. The suggestion was made that 2480 molecules function as a unit to reduce one molecule of carbon dioxide. The mean time for a unit to complete the cycle of photochemical and Blackman reactions was calculated to be between 0.01 and 0.02 second. The existence of such a photosynthetic unit was subsequently detected in work on six plant species.[126] More recently, Kohn [127] by measuring the oxygen production on exposure of green algae to flashes from a neon tube found only 360 molecules of chlorophyll to comprise the photosynthetic unit. Weiss [128] accounts for the existence of the unit by assuming that about 500 molecules in the interior of a lipoid phase absorb and hand on the necessary quanta for one molecule on the surface. He also believes ferrous ions at the surface play a role in the reduction. It may be noted that Franck regards the assumption of photosynthetic units as unnecessary. Weiss also discusses the mode of transfer of excitation energy from molecule to molecule in the complex.[129]

Important studies have recently been made on the course of photosynthesis in certain purple bacteria which promise to throw some light on the evolution of photosynthetic mechanisms. Van Niel [130] observed that some of these organisms require the absorption of but one quantum. On the other hand, French [131] states that the process is similar to that in green plants. Recently, the quantum yield has been found to be much lower, twelve to eighteen quanta (8500-8900 or 5900A) being required to reduce a molecule of carbon dioxide.[132]

The possibility that a chromoprotein as phycoerythrin may act as the sensitizer in the red algae has been discussed by Wurmser [133] and by Moore, Whitley and

[122] Wohl, K., *Z. physik. Chem*, **B37**, 122, 169 (1937).

[123] Baas-Becking, L. G. M., and Hanson, E. A., *Proc. Acad. Sci. Amsterdam*, 40, **792** (1937); *Chem. Abs.*, **32**, 2178 (1938)

[124] Knoll, A F, Matthews, F. L., Jr., and Crist, R. H., *J. Chem. Phys.*, **6**, 109 (1938). For recent kinetic data on photosynthesis, especially the induction period, in single fronds of *Cabomba caroliniana*, see E. L. Smith, *J Gen. Physiol.*, **20**, 807 (1937); **21**, 151 (1937).

[125] Emerson, R., and Arnold, W., *J. Gen. Physiol.*, **16**, 191 (1932).

[126] Arnold, W., and Kohn, H. I., *J. Gen. Physiol.*, **18**, 109 (1934); see also Arnold, W., *Ibid*, **17**, 135 (1933).

[127] Kohn, H. I., *Nature*, **137**, 706 (1936) .

[128] Weiss, J., *J. Gen. Physiol*, **20**, 501 (1937). See also Wohl, K., *Z. physik. Chem.*, **B37**, 105, 186, 209 (1937).

[129] Weiss, J., *Nature*, **141**, 248 (1938).

[130] Van Niel, C. B., *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 138 (1935); *Chem Abs*, **30**, 6782 (1936); Gaffron, H., *Biochem Z*, **275**, 301 (1935); van Niel, C. B., *Bull. assoc diplomes microbiol, faculte pharm. Nancy*, **No. 13**, 3 (1936); Sapozhnikov, D. I., *Biokhimiya*, **2**, 181 (1937); *Chem. Abs*, **31**, 7923 (1937).

[131] French, C. S., *Science*, **84**, 575 (1936); *J. Gen. Physiol.*, **21**, 71 (1937). See also Nakamura, H., *Acta Phytochim. (Japan)*, **9**, 189, 231 (1937); *Chem. Abs.*, **31**, 7465 (1937); *Acta Phytochim. (Japan)*. **10**, 211 (1937); *Chem. Abs.*, **32**, 210 (1938).

[132] Eymers, J. G., and Wassink, E. C., *Enzymologia*, **2**, 291 (1938); *Chem. Abs.*, **32**, 5436 (1938).

Webster.[134] Montfort[135] finds fucoxanthin in brown algae to have a definite physiological function in increasing the photosynthetic efficiency in blue light. Instead of falling off from the red to the blue, it increases in some species to a value three times as high as required by the quantum theory and to more than twice the efficiency in red light. Carotene and xanthophyll in plants in which they are present appear not to have a part in increasing the efficiency.[136] In *Chlorella*, respiration and photosynthesis are retarded by 88 per cent heavy water.[137] Pratt, Craig and Trelease[138] found that although 99.9 per cent heavy water depressed photosynthesis to 41 per cent of that in water in bright light, it showed little difference from water at low light intensities. The lower rate suggested that deuterium exchanges for hydrogen at a critical point in some molecule involved in one of the dark reactions. The respiration is less retarded by heavy water. The temperature coefficients of photosynthesis in H_2O and D_2O were the same in the range 10-30 °C, but higher for D_2O than water between 30 and 46 °C.

Plane-polarized light formed no different amount of starch from that produced by ordinary light in the leaves of *Allium cepa* or *Helianthus annuus*.[139] On the other hand, elliptically polarized light retarded the formation of carbohydrates in leaves.[140] Leaves were also said to absorb a larger amount of energy from polarized than from ordinary light.

It has been suggested that ester formation in plants is due to the ultraviolet rays of sunlight.[141] Pal[142] finds light necessary for not only the conjugation of *Spirogyra*, but also for the conversion of carbohydrates to fats or oils. In darkness, there occurs a conversion of fats to carbohydrates. Our knowledge of the photosynthesis of volatile oils and allied principles is still speculative.[143]

Photosynthesis of Proteins. Baly, Heilbron and Hudson[144] reported that activated formaldehyde, produced photochemically according to the disputed methods of Baly, reacts rapidly with nitrites with the formation of hydroxamic acid, the reaction taking precedence over the polymerization of the formaldehyde to reducing sugars.[145] Formhydroxamic acid is assumed by Baly to react further in various ways with activated formaldehyde to give rise to α-amino acids and nitrogen bases, including even alkaloids. Baly and co-workers believed they had isolated two alkaloids and an amino-acid like histidine formed in this manner in *in vitro*

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[133] Wurmser, R., *Trav. Inst. Physiol. Gen. Strassbourg*, 1919-20, *Chem. Abs.*, **19**, 3289 (1925).

[134] Moore, B., Whitley, E., and Webster, T. A., *36th Ann. Report. Oceanography, (Liverpool)* 1922; *Chem. Abs.*, **19**, 3289 (1925).

[135] Montfort, C., *Jahrb. wiss. Botan.*, **83**, 725 (1936), *Chem Abs.*, **31**, 4693 (1937), Schmidt, G., *Jahrb. wiss. Botan.*, **85**, 554 (1937); *Chem. Abs.*, **32**, 3788 (1938).

[136] See, however, Sapozhnikov, D. I., *Biokhimiya*, **2**, 730 (1937), *Chem Abs.*, **32**, 6673 (1938).

[137] Shibata, K, and Watanabe, A., *Acta Phytochim*, **9**, 107 (1936); *Chem. Abs.*, **30**, 8272 (1936).

[138] Pratt, R., Craig, F. N., and Trelease, S. F., *Science*, **85**, 271 (1937); *Am. J. Botan.*, **24**, 232 (1937); Curry, J., and Trelease, S. F., *Science*, **82**, 18 (1935); Pratt, R., and Trelease, S. F., *Am. J. Botany*, **25**, 133 (1938).

[139] Dastur, R. H., and Asana, R. D., *Ann. Botany*, **46** 879 (1932); *Chem. Abs.*, **27**, 2709 (1933); Johnston, E. S, *Smithsonian Inst. Pub. Misc. Collections*, **96**, No. 3 (1937).

[140] Dastur, R. H., and Gunjikar, L. K, *Ann. Botan.*, **48**, 1003 (1934); **49**, 273 (1935); *Chem. Abs.*, **29**, 1456, 5877 (1935). See, however, Semmens, E., *Nature.*, **134**, 813 (1934); **130**, 243 (1932); *Bot. Gaz.*, **90**, 412 (1930); *Chem. Abs.*, **25**, 983 (1931).

[141] Stoermer, R., and Ladewig, H., *Ber*, **47**, 1804 (1914).

[142] Pal, N. L., *New Phytol*, **33**, 242 (1934); *Chem Abs.*, **29**, 2997 (1935).

[143] Singleton, F., *Chem. & Ind.*, **50**, 989 (1931).

[144] Baly, E. C. C., Heilbron, I. M., and Hudson, D. P, *J Chem. Soc*, **121**, 1078 (1922), *J. Soc. Chem Ind*, **41**, 609A (1922); *Chem Abs.*, **16**, 3463 (1922); Baly, E. C. C., Heilbron, I. M, and Stern, H. J., *J. Chem. Soc.*, **123**, 185 (1923), *Chem. Abs.*, **17**, 1421 (1923).

[145] Either diffused daylight or ultraviolet, according to Baudisch, O., [*Ber.*, **44**, 1009 (1911); **49**, 1176 (1916); **51**, 793 (1918)] causes methanol to react with potassium nitrite, yielding the potassium salt of formhydroxamic acid, CHOH=NOK.

experiments. Snow and Stone,[146] however, pointed out that the identification of these alkaloids had been insufficient, and that certain simpler compounds would yield the tests which had been described.

Burk[147] made over five hundred experiments to detect the formation of complex nitrogen compounds by the action of intense sunlight and colored inorganic catalysts upon ammonia and such carbon compounds as carbon dioxide, formic acid, formaldehyde or dextrose. The results were in general negative. The only type of reaction observed was the oxidation of ammonia to nitrate which occurred in the presence of ferric chloride, or to nitrites and nitrates in the presence of zinc or mercuric oxide. Hydroxylamine and hydrogen peroxide, or complex nitrate compounds were never produced.

Recently, however, Bhargava and Dhar,[148] claimed success in the production of nicotine and methylamine by exposing a small quantity of ammonia and a 2 per cent solution of formaldehyde to a mercury-vapor lamp or to sunlight in the presence of zinc oxide, titanium dioxide or copper carbonate. Dhar and Mukherjee[149] also claimed that a similar exposure of 0.5N solutions of ammonium, potassium or sodium nitrate, containing glucose, tartaric acid, glycerol, arabinose, fructose, mannose or galactose, gave positive colorimetric tests for amino-acids. The yields were best with ammonium nitrate and none were formed in darkness or when ammonium hydroxide was used as the nitrogen source. The amounts of amino-acids reached a maximum in four to six hours, after which they were removed by oxidation.

Urban[150] finds that ammonia nitrogen is taken up by *Chlorella* and other forms more rapidly in light. Loose and Pearsall[151] find that in this organism the velocity of protein synthesis is five times as great in light as in darkness. If sufficient carbohydrate is available, the final equilibrium is similar.[152]

According to Tottingham and Louwsma,[153] a 50 to 400 per cent increase in the blue, violet and long ultraviolet rays increases the absorption of nitrates and to a smaller extent the synthesis of proteins by wheat. When the short wave-length limit is extended from 4000 to 3700A, there is no change. When it is extended to 3000A there is an increase in the absorption but not in the assimilation of nitrates. The admission of rays as short as 2800A decreases the formation of tissue and proteins. Although increasing the proportion of blue to violet light by supplementing Mazda lamps by carbon arcs increases the percentage of protein in young wheat plants, it decreases the pentosans and crude fiber.[154] Solar ultraviolet causes more marked changes and increases the percentage of lipids and of uronic acid.

In tobacco stalks and leaves, light probably leads to a synthesis of glutamine.

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[146] Snow, O. W., and Stone, J. F. S., *J. Chem. Soc.*, **123**, 1509 (1923); *Chem. Abs*, **17**, 2865 (1923).

[147] Burk, D., *J. Phys Chem.*, **31**, 1338 (1927). See also Calcagni, G., *Rev. biol.*, **22**, 92 (1937); *Chem. Abs.*, **32**, 4625 (1938).

[148] Bhargava, L. N., and Dhar, N. R., *J. Indian Chem. Soc.*, **10**, 453 (1933); *Chem. Abs.*, **28**, 413 (1934).

[149] Dhar, N. R., and Mukherjee, S. K., *Nature*, **134**, 499 (1934); *J. Indian Chem. Soc.*, **11**, 727 (1934); *Chem. Abs.*, **29**, 2450 (1935).

[150] Urban, O., *Jahrbuch Wiss. Botan.*, **75**, 1 (1932); *Chem. Abs*, **26**, 4629 (1932).

[151] Loose, L., and Pearsall, W. H., *Nature*, **171**, 362 (1933).

[152] For the blue-green alga, *Nostoc*, see Allison, F. E., and Hoover, S. R., *Trans. 3rd Intern. Congress Soil Sci. Oxford*, **1**, 145 (1935); *Chem. Abs.*, **29**, 8203 (1935).

[153] Tottingham, W. E., and Louwsma, H. W., *J. Am. Chem. Soc.*, **50**, 2436 (1928); Tottingham, W. E., Stephens, H. L., and Lease, E. J., *Plant Physiol.*, **9**, 127 (1934); *Chem. Abs.*, **28**, 3444 (1934).

[154] Tottingham, W. E., and Lease, E. J., *Science*, **80**, 615 (1934); *J. Am. Chem. Soc.*, **57**, 2613 (1935).

Malic acid diminishes and citric acid increases in cultures in darkness. Oxalic acid is unchanged.[155]

Small amounts of ultraviolet light cause an increase in the nitrogen content of *Sinapis alba*.[156]

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[155] Vickery, H. B., Pucher, G. W., Wakeman, A. J., and Leavenworth, C. S., *Conn. Agr. Expt. Sta., Bull.* **407**, 111 (1938); *Chem. Abs.*, **32**, 5441 (1938); *J. Biol. Chem.*, **119**, 369, 523 (1937).

[156] Kabos, W. J., *Rec. trav. botan. neerland.*, **33**, 447 (1936), *Chem. Abs.*, **32**, 212 (1938).

Chapter 44

Effects of Ultraviolet Radiations on Plants

Although de Lima[2] found that ultraviolet light has no effect on germinating rye, others have claimed that, at least in certain wave-length regions, it stimulates germination. DeWolf and Fry[3] proposed to subject seeds before sowing to the action of ultraviolet rays from a mercury-vapor lamp or other source, with or without previous treatment in water or a solution of sodium nitrate or manure. Heinisch[4] believed the germinating power of unripe barley to be considerably improved by ultraviolet irradiation. If, however, the same barley had been allowed to ripen before harvesting, the effect of irradiation was less striking.

Many workers have, however, shown that in general unfiltered mercury arc irradiations are harmful to germinating plants. In the case of dry seeds, lack of penetration of the coats may prevent these effects from becoming readily apparent. There is general agreement that if radiations of wave-length shorter than 2900A are applied, lethal action will result, as discussed in Chapter 33 in the case of bacteria and other organisms.[5]

Some authors have recently claimed that there is a stimulating action of ultraviolet rays longer than the lethal limit. Higgins and Sheard[6] found wave-lengths between 3200 and 3900A transmitted by a Corning ultraglass filter 586 AW, particularly effective in producing germination and growth of cucumber seeds. Rays between 2700 and 3200A delayed the time of germination and reduced the rate of growth.

Gilles[7] believed the germination of lentil and turnip seeds accelerated but their growth somewhat diminished by mercury-arc irradiation. A few other workers claimed to have obtained a stimulating action by filtered ultraviolet, applying wave-lengths in the region of 3650A or those of daylight.[8]

These reports have been criticized by Popp and Brown,[9] largely because the

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[1] The interested reader may find summaries of the extensive work on the effects of visible light in the book edited by Duggar, B. M., "Biological Effects of Radiation," New York, McGraw-Hill Book Company, Inc., 1936

[2] de Lima, P., *Compt. rend.*, **105**, 493 (1930).

[3] De Wolf, C. E., and Fry, H E., British P. 23,339, Oct 15, 1913; *Chem. Abs.*, **9**, 950 (1915).

[4] Heinisch, O., *Wochschr Brau.*, **49**, 348 (1932), *Chem. Abs.*, **27**, 3028 (1933); de Fazi, R., *Atti Acad. Lincei*, **11**, 1022 (1930); *Chem. Abs.*, **25**, 3121 (1931); Kamenskii, K. V., and Orekhova, T A, *Bull Applied Botany, Genetics Plant Breeding (U S.S R.)*, *Ser.* **IV**, No. 2, 67 (1937), *Chem Abs*, **31**, 5843 (1937).

[5] Carl, *Beitr. Biol. Pflanz. (Cohn's)*, **12**, 435 (1914), Sibilia, C, *Bull. soc Bot. Ital.*, 160 (1925) cited by Popp, H. W., and Brown, F., in Duggar, B. M. "Biological Effects of Radiation," New York, McGraw-Hill Book Co., Inc., 1936, II, Chapter 26. Dane, H. R., *Science*, **66**, 80 (1927); Delf, E. M., Ritson, K., and Westbrook, A., *Brit. J. Exptl. Biol.*, **5**, 138 (1927); Cluzet, J., and Kofman, T., *Compt rend soc. biol.*, **101**, 820 (1929).

[6] Higgins, G. M, and Sheard, C, *Plant Physiol.*, **2**, 325 (1927), *Chem. Abs*, **22**, 3685 (1928)

[7] Gilles, E, *Compt. rend. soc. biol*, **109**, 739 (1932); *Chem. Abs*, **27**, 3969 (1933) Gilles reviews work subsequent to 1881 and concludes light less than 2900A favors germination, but affects adult plants adversely The range 2900 to 3100A favors plant development. *Ann. univ. Lyon, Ser* 3, **1C**, 38 (1936); *Chem. Abs.*, **32**, 7965 (1938).

[8] Valentin, H, *Pharm Ztg*, **75**, 982, 995, 1005 (1930); *Chem Abs.*, **25**, 120 (1931); Jacobi, *Beitr. Biol. Pflanz (Cohn's)*, **16**, 405 (1928); Masure, M. P., *Botan. Gaz.*, **93**, 21 (1928); *Chem. Abs.*, **26**, 2487 (1932).

[9] Popp, H. W., and Brown, F, *Bull. Torrey Botan. Club*, **60**, 161 (1933); *Chem. Abs.*, **27**, 2709 (1933); "Biological Effects of Radiation," edited by Duggar, B. M., **II**, 851, New York, McGraw-Hill Book Company, Inc., 1936.

possible effects of infrared rays upon the irradiated plants were not adequately eliminated. Very extensive studies by Popp led to the following generalizations:[10]

1. Exposure of dry seeds to the full ultraviolet of a quartz mercury-vapor arc have little or no effect on later germination and growth, even after 188 hours' exposure. This may be due to inability of the short rays to penetrate the dry seed coat.
2. Exposures of less than two hours' duration on soaked seeds that have not yet begun to sprout did not have a marked effect on germination. Probably here too there is not enough penetration of the short rays in so short a time to cause any permanent injury.
3. Longer exposures to the open arc decrease the rate and the amount of germination, inhibit growth and development and finally cause death of the plant. The wavelengths below 3000A are more effective in this respect than are those above.
4. In general, cotyledons of seeds exposed to ultraviolet seems to have difficulty in emerging from the seed coat, but if they do get through they are not seriously injured by the short rays until after long exposures, 120 hours.
5. Chlorophyll appears in the cotyledons of seedlings raised under the open arc about as rapidly as it does in ordinary light, but never reaches the intensity it does in daylight.
6. Ultraviolet light does not seem to be necessary for a development of the reddish-purple pigment on the under side of the cotyledons of mustard. Under Noviol glass which screens off all ultraviolet and in the dark, this pigment always appears. It reached its deepest intensity uniformly in the greenhouse plant where comparatively little ultraviolet was present.
7. Geranium plants exposed to the open arc for 6 hours, after being in the dark for 24 hours showed no difference in appearance at the end of the 6 hours, but tests of the leaves for starch at this time were entirely negative. But in ordinary light, starch can be located in these leaves after an hour or less.
8. In no case were new leaves formed in mustard under ultraviolet rays. The new leaves were formed in sunflower, Canada field peas, oats and corn, but these leaves were all killed in a day or two after they were formed.
9. A few plants were able to grow under the open arc in all of the series but in no case was there any further development than would result from the food stored in the seeds.
10. Seedlings that do not survive will live longer under its rays than those grown in the dark at the same time. Since there is apparently very little food synthesis, this may be due to a retarding of enzyme action or other germination processes. If these seedlings after being exposed from 6 to 8 hours a day for 10 to 15 days are removed to the greenhouse, they immediately start to develop normally; but exposed seeds that have not germinated under ultraviolet rays cannot be made to germinate in this way later.
11. Seedlings grown in daylight in the absence of ultraviolet or in complete darkness and then exposed to the open arc were killed after 6 to 20 hours' exposure. Similarly, the leaves of mature plants of geranium or coleus with 6 hours' exposure to the open arc will have a burnt appearance the next day and fall off. In the seedlings, the young leaves and next the stems are most susceptible to injury. Apparently, those grown under the arc from the start are able to adapt themselves to it to a certain extent. Finally, of course, they too are killed.
12. When all ultraviolet was screened off, mustard seeds in visible light gave as high a rate and amount of germination as they did in complete darkness. This same effect was produced, however, when the seeds were exposed to all the rays between 6000 and 3000A. If the ultraviolet between 3000 and 4000A was the only radiation falling on the seeds, a somewhat lower rate and amount of germination were observed. Apparently, the inimical effects of the regions between 4000 and 3000A are overcome when visible light is falling on the plants at the same time.
13. No striking differences in growth and development of seedlings of mustard were observed when all ultraviolet was screened off, as compared with seedlings grown under the rays from 6000 to 3000A. If, however, the region between 4000 and 3000A was the only one to which the seedlings were exposed, a distinct retarding of growth and development occurred.
14. Bacteria and general damping-off fungi do not develop in the rays of the open arc but will if the region below 3000A is screened off.

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[10] Private communication from Prof. H. W. Popp.

More Mature Plants. A large number of investigations have been devoted to the determination of the effects on growth which may be ascribed to the ultraviolet portion of the solar spectrum. Maquenne and Demoussy[11] early stated that ultraviolet rays properly applied are very beneficial to flowers and other vegetation. In various species, Tottingham and Moore[12] found seed production, root storage or earliness of blooming were favored by irradiation under Vitaglass as compared with common glass. Certain species which do not possess winter hardening capacities were more subject to frost injury following early development under this glass. In some instances an increase in the percentage of protein or non-protein, non-lipid nitrogen was found in the tissues produced under Vitaglass. The most consistent compositional response to this irradiation was believed to be an increased percentage of lipids in the dry matter, but this was not very definite. Similar results were also reported for tomato seedlings by Tottingham,[13] using a General Electric sunlamp. Popp[14] believes that, although ultraviolet rays are not indispensable, the blue-violet end of the visible spectrum is necessary for the normal, vigorous growth of the plant.

Subsequently, Popp and Brown[15] reviewed a number of papers in which a stimulating effect of the ultraviolet longer than 2900A had been claimed. It is scarcely necessary to discuss these here. In practically all of them it was possible to find flaws in the methods employed. Arthur,[16] at the Boyce Thompson Institute was unable to find that the use of ultraviolet-transmitting glasses offered any advantages in plant growth.

Singh, Kapoor and Choudhri[17] found exposure of plants to ultraviolet rays for periods of five minutes or more at intervals of less than 14 days to be detrimental to growth.

Ultraviolet produces growth inhibition and morphological changes in Aspergillus, according to Kresling and Shtern.[18]

The growth substance, 3-indolepropionic acid, turns yellow under ultraviolet irradiation and acquires an unpleasant odor. At the same time the blue fluorescence of its acid solutions decreases, as does its ultraviolet absorption band. After several hours of irradiation, the solution loses its ability to retard the root growth of corn and bean roots in Knop's solution.[19] Similarly, the growth substance in oat coleoptiles loses its activity when intensely irradiated with a mercury arc.[20]

The formation of chlorophyll is favored by visible light of low intensities; high intensities of light tend to destroy it. Relatively few observations have been made on the influence of ultraviolet light upon its formation. According to Tottingham,[21] tomato leaf tissue grown under glass and under Vitaglass showed respectively, chlorophyll 1.76 and 1.50 per cent, carotene, 0.007 and 0.017 per cent, and xanthophyll 0.053 and 0.368 per cent. From the lipid fraction, there were obtained sterols to the extent of 0.81 and 0.87 per cent. The conclusion was that the formation of carotenoids and sterols is favored by irradiation under Vitaglass, but the chlorophyll declines. The ratio of chlorophyll-*a* to chlorophyll-*b* is lowered by irradiating leaves with monochromatic light largely absorbed by chlorophyll-*a*.[22]

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[11] Maquenne, L., and Demoussy, E., *Compt. rend.*, **149,** 756 (1909).

[12] Tottingham, W. E., and Moore, J. G., *J. Agr. Research,* **43,** 133 (1931); *Chem. Abs.,* **25,** 5913 (1931).

[13] Tottingham, W. E., *Plant Physiol.,* **7,** 551 (1932).

[14] Popp, H. W., *Am. J. Botan.,* **13,** 706 (1926); *Chem. Abs.,* **22,** 3191 (1928); *Botan. Gaz.,* **82,** 306 (1926); *Chem. Abs.,* **21,** 435 (1927). See also Arthur, J. M., and Harvill, E. K., *Contrib. Boyce Thompson Inst.,* **8,** 433 (1937); *Chem. Abs*, **31,** 6285 (1937).

[15] Popp, H. W., and Brown, F., "Biological Effects of Radiation," edited by Duggar, B. M., II, 853, New York, McGraw-Hill Book Company, Inc., 1936.

[16] Arthur, J. M., *Sci. Monthly,* **31,** 343 (1930); Arthur, J. M., and Newell, J. M., *Am. J. Botan.,* **16,** 338 (1929).

[17] Singh, B. N., Kapoor, G. P., and Choudhri, R. S., *Botan. Gaz.,* **97,** 649 (1936); *Chem. Abs.,* **30,** 4197 (1936).

[18] Kresling, E. K., and Shtern, E. A., *Zentr. Bakt. Parasitenk.,* **II Abt. 95,** 327 (1936), *Chem. Abs.,* **30,** 5256 (1936).

[19] Hare, D., and Kersten, H., *Plant Physiol.,* **12,** 509 (1937).

[20] Burkholder, P. R., and Johnston, E. S., *Smithsonian Misc. Coll.,* **95,** No. 20 (1937).

[21] Tottingham, W. E., *Science,* **75,** 223 (1932); *Chem. Abs.,* **26,** 2488 (1932).

Colla [23] ascribes the formation of chlorophyll in wheat, beans and lentils to the action of radiations in the range 3300 to 3900A, without the aid of visible rays.

Stoklasa [24] early observed that after irradiation by wave-lengths 3000 to 5000A (mercury arc), the young leaves of the etiolated seedlings of *Pisum, Zea mais, Avena* and *Hordeum* showed a dark green coloration in two hours. With solar irradiation a similar color was formed only after six hours of exposure. He also believed that chlorophyll exerts a protective action against ultraviolet rays of daylight. The cells of flowers as well as those of plants grown under glass were more sensitive toward ultraviolet rays than the cells of green leaves. Jirovec [25] finds the chlorophyll-free stems of *Euglena gracilis* considerably more sensitive to ultraviolet rays than are green stems of the same species. Dangeard [26] found the energy of wave-lengths shorter than 4900A from a Nernst lamp incapable of aiding the formation of chorophyll, but Sayre [27] has found that if the intensity is high enough chlorophyll may be developed by the wave-length region 3000 to 4000A. The function of the ultraviolet is still, however, uncertain.[28]

A colorless protochlorophyll may be present in sunflower seedlings grown in the dark, but etiolated plants must be irradiated before chlorophyll can form in them.[29] Beck finds that xanthophyll and carotene are formed in the dark. However, light may stimulate the production of these pigments.[30]

Certain acid-fast bacteria produce pigment in darkness only after brief preceding exposures to ultraviolet light or longer exposures to incandescent lamp light.[31]

Wave-lengths in the region 2900 to 3100A were believed by Benedict [32] to increase the dry weights of a number of plants, but not of corn. They also cause an increase in the calcium content, but the results with phosphorus were inconclusive. Wynd and Fuller [33] observed that when tomato and cucumber plants were irradiated daily through Vitaglass at 100 inches from an arc, after five weeks there was an increase in the calcium content as compared with that in controls. The phosphorus content decreased. Experiments of this type were conducted to determine whether sterols in the plant could be converted into a vitamin which aids the absorption of calcium by the plant as in the case of vitamin D in animals. According to Stewart and Arthur,[34] tomato, tobacco, datura, lettuce, and salvia, grown in periods of low light intensity and then irradiated by a quartz mercury arc, showed an increase in ash, and in calcium or phosphorus or both. If, however, the plants were grown in light of high intensity, they failed to exhibit these changes on irradiation. Cabbage did not show these changes. It responded at first by an increase in ash in the leaves and a decrease in the stem. Repeated irradiations caused an increase of ash of stem and leaves and an increase in calcium or phosphorus or both. The manganese and magnesium contents of plants were not affected by ultraviolet irradiation. Similar ash changes could be obtained by treating the plants with irradiated ergosterol.

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[22] Tottingham, W. E., and Dutton, H. J., *Science,* **87,** 214 (1938).

[23] Colla, S., *Boll. soc. ital. biol. sper.,* **4,** 298 (1929); *Chem Abs.,* **23,** 4496 (1929).

[24] Stoklasa, J., *Strahlentherapie,* **6,** 119 (1915); *Zentr. Biochem. Biophys.,* **18,** 370 (1915).

[25] Jirovec, O., *Protoplasma,* **21,** 577 (1934); *Chem. Abs ,* **28,** 6765 (1934).

[26] Dangeard, P. A., *Botaniste,* **12,** xxii (1912). Cited in Duggar, B. M., "Biological Effects of Radiation," New York, McGraw-Hill Book Co., Inc., 1936.

[27] Sayre, J. D., *Plant Physiol.,* **3,** 71 (1928).

[28] See also Shirley, H. L., *Am J. Botany,* **16,** 354 (1929).

[29] Beck, W. A., *Studies Inst. Divi Thomae,* **1,** 109 (1937); *Protoplasma,* **28,** 273 (1937); *Plant Physiol.,* **12,** 885 (1937); Vogele, A. C , *Ibid.,* **12,** 929 (1937).

[30] Beck, W. A., *Studies Inst Divi Thomae,* **1,** 217 (1937); Beck, W. A., Redman, R., and Schroeter, M. P., *Ibid ,* **1,** 245 (1937). See also Seybold, A., and Egle, K., *Planta,* **28,** 87 (1938); *Chem Abs.,* **32,** 5443 (1938); Strain, H. H , *Plant Physiol ,* **13,** 413 (1938). *Chem Abs.,* **32,** 8476 (1938); Strott, A., *Jahrb. wiss. Botan.,* **86,** 1 (1938); *Chem. Abs.,* **32,** 8482 (1938).

[31] Baker, J. A., *J. Bact.,* **35,** 625 (1938).

[32] Benedict, H. M., *Botan Gaz ,* **96,** 330 (1934); *Chem. Abs.,* **29,** 1131 (1935).

[33] Wynd, F. L., and Fuller, H J., *Ann. Mo. Botan. Gardens,* **18,** 565 (1931); *Chem. Abs.,* **26,** 2215 (1932).

Tomato plants previously grown on solutions lacking calcium or phosphorus showed no increase in ash, calcium or phosphorus on irradiation with a quartz mercury arc. The level of the supply of these elements and not their ratio determines the response to irradiation. In solutions low in phosphorus and high in calcium, irradiation increases the ash and calcium. In solutions low in calcium and high in phosphorus, the ash and phosphorus increased.[35]

In experiments of Mitchell,[36] equal amounts of radiant energy from a 3000-watt carbon arc and a 2000-watt Mazda incandescent lamp were supplied for two weeks to tomato plants. Those under the arc grew less in height and synthesized more than twice as much solid matter and approximately four times as much acid-hydrolyzable materials and sugars as did those under the incandescent lamp. For equal incident energy, the arc was 53 per cent more efficient in electrical energy consumption in producing dry matter. But when the light from the two sources was balanced by a photronic cell, there was a more equal gain in dry weight and carbohydrates under both sources. Those plants under the arc then synthesized less solid matter per unit of time than did those under the incandescent lamp.

But little work has been done on the effect of ultraviolet on the respiration of plants. Masure[37] claimed that the region near 3650A, obtained by the use of a Corning G586AW filter, temporarily accelerates the respiration of pea seedlings. His work has, however, been criticized by Popp and Brown[38] on the ground that the filter used transmitted also infrared radiations and that these, rather than the ultraviolet, may have been the cause of the effects observed. Wynd, Fuller and Reynolds[39] believe that injurious raying of tomato plants stimulates respiration and peroxidase and, in general, catalase, but inhibits oxygenase. Non-injurious raying stimulated catalase. Comparatively weak irradiation of bean plants stimulated peroxidase.

Percival[40] finds that exposure to light coming through window glass causes a darkening of the mycelium of the fungus, *Fomes pini*. Exposures to ultraviolet rays of sunlight in addition to the visible spectrum caused a further darkening of the mycelium and a suppression of aerial hyphae. Stephens [41] finds ultraviolet irradiation of certain strains of the fungus *Glomerella* greatly stimulated conidial production. Certain strains which had never been known to produce perichecia did so after irradiation if either pepsin, raffinose or magnesium sulfate was added to the nutrient medium.[42]

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[34] Stewart, W. D, and Arthur, J. M., *Contrib. Boyce Thompson Inst.*, **6**, 225 (1934); *Chem. Abs.*, **28**, 5853 (1934).

[35] Stewart, W. D., and Arthur, J. M., *Contrib. Boyce Thompson Inst*, **9**, 105 (1937); *Chem. Abs.*, **32**, 1756 (1938).

[36] Mitchell, J. W., *Botan. Gaz.*, **99**, 412 (1937); *Chem Abs*, **32**, 1759 (1938).

[37] Masure, M. P., *Botan Gaz.*, **93**, 21 (1932); *Chem. Abs.*, **26**, 2487 (1932).

[38] Popp, H. W., and Brown, F., *Bull Torrey Botan. Club*, **60**, 161 (1933), *Chem. Abs.*, **27**, 2709 (1933).

[39] Wynd, F. L., Fuller, H. J, and Reynolds, E. S., *Ann. Missouri Botan. Gardens*, **22**, 837 (1935); *Chem Abs*, **30**, 3466 (1936).

[40] Percival, W. C., *Bull. N. Y. State Coll. Forestry*, **6**, IB, 72 pp. (1933); *Chem. Abs.*, **29**, 2573 (1935).

Some applications of ultraviolet light in the treatment of plant diseases have been noted by Pichler and Wöber,[43] but x-rays were more efficient.

Attempts are being made in the U.S.S.R. to induce the formation of rubber in plants by treating them with ultraviolet rays. Novikov and Herber [44] soaked seeds of the Tau-sagyz rubber plant in distilled water for 18 hours at 25°C., dried and irradiated them with a quartz mercury arc under varying conditions. After irradiation, the seeds were allowed to germinate at 25°C. for two days, after which the catalase activity was determined. In all irradiated seeds the catalase activity increased abruptly. Ultraviolet irradiation of the leaves of Tau-sagyz and Asclepias, previously saturated with 3-per cent sucrose solutions, caused these plants to continue the formation of rubber in the dark in a 3-per cent sucrose solution. Non-irradiated leaves, either saturated or unsaturated with sugar, not only formed no new rubber in the dark but even lost that which they had contained. Irradiated leaves not saturated with sugar did not produce any rubber.

During growth, plants from irradiated seeds were said not to have been attacked by aphids; they also shed their leaves later and recovered their foliage earlier, indications of increased life tonus.

From microchemical observations, Kiselev, Osipov and Kuz'mina,[45] concluded that the formation of rubber and closely related resinous material is a photosynthetic process.

Exposure of apples to ultraviolet light produced injury and discoloration of the anthocyanins, according to Pearce and Streeter.[46] Freytag [47] finds that ultraviolet rays may produce necrotic pigmentation (probably melanin) in leaves and fruit skins. Oxygen is necessary for this. With certain leaves a change in permeability seems to result.

No significant increase in the glucoside yield could be obtained by growing digitalis plants under glass transparent to ultraviolet rays, according to recent experiments of Leonard and Arthur [48] which thus failed to confirm the prior claims of McCrae that this could be done.[49]

Potato tubers irradiated for twenty days with a Uviol mercury arc or by Mazda lamps showed an increased solanine content, accompanied by the appearance of anthocyanin in the sprouts. Irradiation with red-orange light did not induce a significant increase in solanine but caused an increase in chlorophyll. Ultraviolet rays of about 3000A were believed to be effective in solanine formation.[50]

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Results on the effect of ultraviolet rays on the changes in water, total and reducing sugars, and malic acid during the ripening of green-picked apples, peaches, pears and plums were irregular, according to Leonicini and Rogai.[51] In some experiments, the total sugar was reduced (one-tenth to one-sixth) by irradiation.

Ultraviolet light (particularly of wave-length 2980A) causes browning of banana skins exposed in air but not in pure carbon dioxide. The effect is inhibited by hydrogen cyanide for wave-lengths less than 3200A, but the effect of the 3800A line is activated by a little hydrogen cyanide and inhibited by an excess. Enzymes of respiration may be involved in the effects.[52]

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